

CONTROL OF HYDROGEN SULPHIDE, AMMONIA AND ODOUR
EMISSIONS FROM SWINE BARNs USING
ZINC OXIDE NANOPARTICLES

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ABSTRACT

Application of zinc oxide (ZnO) nanoparticles was evaluated as a possible measure to mitigate the levels of hydrogen sulphide (H_2S), ammonia (NH_3) and odour in swine facilities. Two deployment techniques were investigated: direct mixing of zinc oxide nanoparticles into the slurry, and filtration with nanoparticles as filtering media for the manure gases. The overall goal of this work was to determine the impact of the treatments on hydrogen sulphide, ammonia and odour emissions, pig performance and manure characteristics as well as to assess the feasibility of the application of this technology in a typical swine barn.

Semi-pilot scale tests were conducted to evaluate operational factors in open system conditions, the results of which showed that the mixing method required a particle-to-slurry ratio of 3 grams of zinc oxide per litre of slurry to control hydrogen sulphide and ammonia levels. Using the air filtration technique, a fluidized bed filter design with a 0.28 g/cm^2 loading rate and rated at 0.5 m/s face velocity was found to be the most effective combination for controlling gas levels. Room-scale experiments were conducted in specially designed chambers to assess the effectiveness of the treatments under conditions that represent commercial swine production. The addition of zinc oxide nanoparticles into the manure achieved more than 95% reduction in hydrogen sulphide levels while no significant effects on ammonia concentrations were observed. Zinc oxide nanoparticles were persistent in maintaining low hydrogen sulphide levels up to 15 days after treatment application. On the other hand, the ventilation air recirculation system with a zinc oxide filter achieved significant reduction in both hydrogen sulphide and ammonia

concentrations at the animal- and human-occupied zones. Neither treatment had any significant impact on pig performance and manure nutrient characteristics. Estimates of the cost of application of the treatments in a 100-head grow-finish room showed that employing the air filtration method amounted to around 3.8% of the average total cost of production, which was economically more feasible than the mixing method; however, various options can be pursued to further reduce the cost of application of both treatments.

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1 INTRODUCTION

Over the last few decades, livestock production systems have shifted towards intensified operations with increasing number of animals being raised in large specialized facilities. Swine production also followed this trend, a consequence of which is the generation of large volumes of manure in intensive swine confinement units from which significant amounts of air contaminants are emitted. These emissions are contributed largely by gases produced from fresh or deposited animal manure (Hartung and Phillips, 1994), of which the gases of greatest concern are ammonia and hydrogen sulphide (Watts, 1999).

Ammonia (NH_3) is formed by bacterial and enzymatic breakdown of nitrogen-containing compounds in the animal manure while hydrogen sulphide (H_2S) is the product of anaerobic decomposition of sulphur-containing amino acids in the feces (Hartung and Phillips, 1994). The emission of these gases is a continuing concern for the swine industry because of their associated negative effects on human and animal health as well as on the environment (Casey et al., 2006). It has been documented that exposure to specific gases in swine facilities can cause illnesses or injuries to both animals and humans, and even fatalities at extreme levels of exposure (ASABE, 2005b). Hog farmers have been reported to experience inflammatory effects on the respiratory system when exposed to 100 ppm of ammonia and/or 200 to 300 ppm of hydrogen sulphide (ASABE, 2005b). In addition, animals exposed continuously to significant amounts of gas may start to develop pneumonia and respiratory diseases (ASABE, 2005b). Several studies have also shown that ammonia-containing exhaust air when oxidized with various compounds in the

atmosphere contributes to environmental acidification (Hartung and Phillips, 1994; Xue et al., 1998; Seedorf, 2004; Casey et al., 2006).

To mitigate the potential risks associated with gas and odour emissions, rigorous regulatory standards have been imposed by the government. In Saskatchewan, the Occupational Health and Safety Regulations have set contamination limits for 8-hour and 15-minute exposures to various gases. Exposure limits for ammonia have been set at 25 ppm (8-hour) and 35 ppm (15-minute). Threshold limits for 8-hour and 15-minute exposures to hydrogen sulphide, on the other hand, are 10 ppm and 15 ppm, respectively (Saskatchewan Labour, 1996).

To meet the minimum requirements as well as to address health and environmental concerns, numerous mitigation techniques ranging from controlling the gas precursors to treating the gases biologically or chemically before releasing to the environment have been explored. These practices include the use of manure additives and biofiltration, among other things. Manure additives have been categorized by McCrory and Hobbs (2001) into pH modifiers and acidifiers, disinfectants, digestive additives, oxidizing agents, enzyme inhibitors, masking agents and counteractants, and adsorbents. Most of these additives have not been fully implemented at the farm scale due to some inconsistencies with regard to their effectiveness in improving air quality in pig houses. Additives such as acidifiers were effective in reducing ammonia concentrations (Hendriks and Vrielink, 1997; Smith et al., 2004) but their application may also favour the formation of hydrogen sulphide, thereby increasing its emission (Shah et al., 2007). Also, some additives were not cost-effective and may require frequent application (McCrory and Hobbs, 2001). Biofiltration, on the other hand, follows the principle of a biological air filtration system (Hartung et al., 2001). The use of biofilters, though has been shown to attain considerable reduction in gas and odour emissions, has not been well adopted by swine farmers. The main

downsides of a biofilter system are their high operating costs in supplying high air flow (Riskowski, 2004), and the need to continuously provide a favourable environment for microbial growth (Nicolai and Janni, 2001). With the drawbacks of existing gas mitigation strategies, the problem of gas and odour emissions from swine farms still persists.

Recently, nanotechnology has been increasingly gaining interest in various areas of research and applications including environmental analysis, treatment and remediation. This technology, in general, utilizes materials with a scale of 1 to 100 nanometres (nm) in at least one dimension such as nanotubes, nanowires and nanoparticles (EPA, 2007). With their inherent properties such as high surface area, high reactivity, and high mobility, these materials have been used as reactive agents (i.e. adsorbents, catalysts, etc.) in treating various environmental pollutants. In studies conducted by Elliot and Zhang (2001) and Varadhi et al. (2005), injection of nanoparticles into groundwater was reported to be an effective remedial technique for reducing contaminants such as trichloroethene (TCE) and chlorinated hydrocarbons. Additionally, several studies revealed the potential application of nanoparticles in drinking water purification and air filtration systems due to their potential for bacterial removal, germ-sterilization and disintegration of hazardous organic materials (Nonami et al., 2004; Jain and Pradeep, 2005; Kim et al., 2006). While some of these applications are already fully developed, exploring the possibilities of using nanotechnology in addressing issues regarding gas and odour emissions from swine facilities has just started.

Bench-scale tests have been conducted on the use of nanoparticles in controlling the emissions of hydrogen sulphide, ammonia and odour from swine manure (Asis, 2008). The study involved the selection of the most promising commercial nanoparticles and possible deployment methods. Using a fully controlled small-scale test set-up, it was shown that mixing and filtration

methods using zinc oxide (ZnO) nanoparticles have great potential to significantly reduce the concentrations of hydrogen sulphide, ammonia and odour from manure slurry (Asis, 2008). Thus, in this study, the effectiveness of these treatment approaches was investigated under commercial barn production conditions. Semi-pilot scale tests were conducted in an open system environment while room-scale tests were done in specially designed chambers. In addition, the impact of the treatments on pig performance and manure characteristics was also monitored. A preliminary cost study was then conducted following the room experiments.

2 LITERATURE REVIEW

2.1 Gas and Odour Emissions from Swine Barns

In livestock housing facilities, gases and odours are generated from feed and animals, and from the excreta; majority of which comes from freshly deposited or stored fecal matter (Hartung and Phillips, 1994). Thus, this study focused on controlling gases and odour produced and emitted from swine manure.

Swine manure consists of about 10% solids and 90% water when excreted by the animals (ASABE, 2005a). It is primarily a mixture of urine and feces, and is classified as slurry based on its dry matter content (MWPS, 2004). Manure characteristics as excreted vary significantly from one barn to the other depending on the management practices and animal age (MWPS, 2004). However, for most barns, it is a common practice to temporarily deposit and accumulate excreted manure in pits. Storing manure in pits would eventually alter its characteristics as a result of water addition, drying, volatilization, and other physical, chemical and biological processes (ASABE, 2005a). According to Zhang et al. (1990), manure in pits has three distinctive zones: the aerobic zone which is in direct contact with the air, the micro-aerobic zone and the anaerobic zone. Each zone undergoes several processes and decomposition which are responsible for the production of different types of gases (Zhang et al., 1990).

2.1.1 Production and characteristics of hydrogen sulphide, ammonia and odour

Among the different gas compounds found in swine facilities, ammonia and hydrogen sulphide are of foremost concern (Watts, 1999). Along with these gases are odorous compounds such as organic acids, amines, carbonyls, phenols, skatols, sulphides and mercaptanes (Simensen, 1987; O'Neill and Phillips, 1992).

Ammonia (NH_3) is produced mostly by bacterial and enzymatic decomposition of protein components in the animal waste, while some are also produced by the animals (Hartung and Phillips, 1994). It is a colorless, highly water soluble gas which can be readily lost to the air by volatilization (ASABE, 2005b). Ammonia is lighter than air and has a pungent odour with a human detection level between 0.5 and 54 ppm (ASABE, 2005b). In well-ventilated animal housing, ammonia levels are typically about 5 to 10 ppm (slatted floors) and 10 to 20 ppm (solid floors), and can periodically exceed 25 ppm during winter conditions (Jacobson et al., 2003).

Hydrogen sulphide (H_2S), on the other hand, originates from the anaerobic bacterial breakdown of sulphur-containing amino acids in the manure (Hartung and Phillips, 1994). It is colorless, heavier than air, highly soluble in water and can be easily detected at very low concentrations because of its characteristic rotten egg odour (ASABE, 2005b). In normal barn operations, levels of hydrogen sulphide are very low compared with the concentrations of ammonia (Casey et al., 2006), but they can reach dangerous levels of 200 to 1000 ppm within a few minutes of agitating or pumping manure (ASABE, 2005b).

As reported by Patni and Clarke (2003), Table 2.1 summarizes the characteristics and exposure limits of manure gases. Exposure limits are expressed in terms of immediately

dangerous to life or health (IDLH) and threshold limit values (TLV). TLV have been categorized into time-weighted average (TWA) which is normally for 8 hours of continuous exposure and the 15-minute short-term exposure limit (STEL).

Table 2.1. Characteristics and exposure limits of hydrogen sulphide and ammonia.

Manure Gas	Characteristics		Exposure limits, ppm			Source
	Specific Gravity	Odour	TLV-TWA	TLV-STEL	IDLH	
Hydrogen sulphide	1.2	rotten egg	10	15	100	OSHA ¹ , 2001
Ammonia	0.6	pungent	25	35	300	NIOSH ² , 2002

¹OSHA: Occupational Safety and Health Administration

²NIOSH: National Institute for Occupational Safety and Health

One hundred sixty-eight odorous compounds have been identified in livestock facilities; 30 of which have an odour detection threshold equal or below 0.001 mg/m³ (O'Neill and Phillips, 1992). Moreover, six of the ten compounds with the lowest odour detection thresholds are sulfurous in nature, thus odour in pig barns has usually been associated with the smell of rotten eggs (O'Neill and Phillips, 1992). These odorous compounds originate from protein sources within the animal's intestine and in the slurry (Hammond et al., 1989). Mackie et al. (1998) studied the biological origins of four classes of odorous compounds including volatile fatty acids (VFA), ammonia and volatile amines, indoles and phenols, and the volatile sulphur-containing compounds. They reported that anaerobic degradation of manure generates the most odorous compounds and these can absorb to dust, clothing and building surfaces. Through processes in the hindgut of pigs, organic matter in feed is converted into volatile fatty acids, while microbial biomass and fermentation gases such as carbon dioxide and methane are also

produced (Mackie et al., 1998). Deamination of amino acids in the gastrointestinal tract and in manure results in the production of volatile fatty acid, carbon dioxide, hydrogen gas, ammonia, indoles and phenols. Sulphur-containing compounds are produced from sulphate reduction and metabolism of sulphur-containing amino acids (Mackie et al., 1998). Thus, as identified by Hobbs et al. (1998), sulphide, volatile fatty acid, phenolic and indolic chemical groups are the primary malodorous compounds in animal buildings.

2.1.2 Impact of hydrogen sulphide, ammonia and odour emissions

The emission of hydrogen sulphide, ammonia and odour from swine facilities has been an impediment to the expansion of the industry due to the following negative impacts of these emissions on human and animal health as well as on the environment.

2.1.2.1 Effects on animals and humans

Manure gases confined in swine buildings are likely to cause health problems to both pigs and farm workers (Donham et al., 1977; Simensen, 1987). Prolonged exposure to gases can reduce pigs' resistance to pathogens which consequently cause diseases (Holyoake, 2005). Following an uninterrupted exposure to 20 ppm of hydrogen sulphide, pigs may develop fear of light and loss of appetite while some respiratory diseases may arise when in contact with 50 ppm of ammonia for prolonged periods (Table 2.2). These symptoms could eventually lead to the pigs' stunted growth, reduced performance, acute toxic conditions and even, death (Simensen, 1987). Bushee et al. (1999) reported that high ammonia levels could decrease food intake resulting to weight loss and increased susceptibility to sickness. Experiments of Holyoake (2005) revealed that respiratory diseases in pigs are due to *Bordetella bronchiseptica* and *Pasteurella multocida* infections brought about by excessive exposure to atmospheric ammonia.

Table 2.2. Effects of hydrogen sulphide and ammonia on pigs at various concentrations (ASABE, 2005b).

Hydrogen sulphide		Ammonia	
Concentration, ppm	Effects	Concentration, ppm	Effects
20	develop fear of light, loss of appetite, and nervousness	50	respiratory diseases with added risk of secondary infections
50-240	vomiting, nausea, and diarrhea	75	induce an unhealthy appearance
800	sudden nausea and unconsciousness followed by death	100-200	induces sneezing, salivation and loss of appetite

As reported by Iversen et al. (1988), swine farmers have higher incidence of occupational respiratory symptoms than any other agricultural workers. This was attributed to continuous exposure to hog barn air (Charavaryamath and Singh, 2006). As shown in Table 2.3, swine workers are likely to experience respiratory tract infections when exposed to 200 - 300 ppm of hydrogen sulphide or 100 ppm of ammonia. These could eventually result to lung dysfunction together with headaches, muscle aches, colds, pains and pneumonia (Simensen, 1987). Also, exposure to more than 500 ppm of hydrogen sulphide or 1000 ppm of ammonia even for a short period can be fatal to humans (ASABE, 2005b). In addition, Schiffman (1998) reported that odours can cause irritation of the eyes, nose and throat as well as drowsiness, and may potentially affect mood and memory of exposed workers.

Table 2.3. Physiological responses of humans when exposed to various concentrations of hydrogen sulphide and ammonia (ASABE, 2005b).

Hydrogen sulphide		Ammonia	
Concentration, ppm	Effects	Concentration, ppm	Effects
0.005	barely detectable		
4	easily detectable; moderate odour		
10	eye irritation		
27	unpleasant odour	50	eye irritation
100	coughing, eye irritation, loss of smell after 2-15 min exposure	100	respiratory tract infection
200-300	eye inflammation and respiratory tract infection after 1 hr		
500-700	loss of consciousness and possible death in 30-60 min		
800-1000	rapid unconsciousness, cessation of respiration and death	1000-1500	fatal levels
1000	diaphragm paralysis on first breath, rapid asphyxiation		

2.1.2.2 Effects on the environment

Among all the trace gases found in swine buildings, ammonia was found to pose the most significant adverse impact on the environment (Hartung and Phillips, 1994). Various studies have shown that ammonia released to the atmosphere has been associated with ecological hazards which include necrosis of leaves, soil acidification, and eutrophication of ground and surface waters through nitrogen enrichment (Hartung and Phillips, 1994; Seedorf, 2004; Casey et

al., 2006). Ammonia emitted from swine buildings could be transported long distances through the air and adsorbed onto surfaces such as leaves and buildings (Hartung and Phillips, 1994). Volatilized ammonia in the air, when oxidized, produces nitrous oxides, which consequently contributes to acid rain (Xue et al., 1998). On the other hand, the compounds adsorbed onto surfaces can be leached by rain water into the soil (Hartung and Phillips, 1994). Excessive nitrogen deposition in the soil alters the normal flow of the ecosystem by favoring nitrogen-indicator plants while restraining the growth of plants that prefer low-nitrogen soils (Hartung and Phillips, 1994). Also, soils get acidified after the nitrification process which leads to the leaching of nutrients and aluminum ions into ground and surface waters, thus contributing to eutrophication (Hartung and Phillips, 1994; Casey et al., 2006).

2.1.3 Practices used to control hydrogen sulphide, ammonia and odour emissions from swine buildings

Several technologies have been evaluated by various researchers and some of them have been adopted by the swine industry to reduce gas and odour levels in livestock facilities. These technologies may be classified as practices that prevent the production of gases in the manure such as diet manipulation and manure additives or strategies that reduce gas levels after being emitted from swine manure which include oil sprinkling and biofiltration.

2.1.3.1 Diet manipulation

The composition of feed introduced to pigs can be modified and reformulated to lessen the presence of gas and odour precursors (ASABE, 2007). Some modifications involved altering the protein and synthetic amino acid levels, and specific nonstarch polysaccharides (soybean hulls and sugar beet pulp) content in diets to reduce nitrogen excretions and consequently

minimize the production of ammonia and other odorous compounds such as hydrogen sulphide (Sutton et al., 1999).

In a study by DeCamp et al. (2001), the addition of 10% soybean hulls and 3.4% supplemental fat to a 12% crude protein (CP) corn-soybean diet reduced aerial ammonia, hydrogen sulphide and odour detection threshold by about 20, 32 and 11%, respectively. Furthermore, Kendall et al. (1999) revealed that reducing dietary crude protein from 13.1 to 9.7% and adding 10% soybean hulls can significantly lower ammonia concentrations by about 40%. In a subsequent study (Kendall et al., 2000), almost 50% reduction in ammonia and hydrogen sulphide was achieved when a reduced crude protein diet (by 3.25%) with 5% added soybean hulls was fed to pigs. However, in a study by Godbout et al. (2001), the use of low-protein diets decreased ammonia levels up to 38% but increased odour emission.

The economic concerns due to cost of new diet formulations have hindered adoption of this technology in commercial swine barns. In addition, considering that gases and odour are also by-products of anaerobic decomposition, altering the properties of fresh manure alone does not solve the issue of gas and odour emissions from swine barns (ASABE, 2007).

2.1.3.2 Manure additives

Additives are substances applied to manure to lessen the extent of odour and gas emissions from livestock barns (McCrory and Hobbs, 2001). Manure additives have been categorized into: (1) pH modifiers and acidifiers, (2) oxidizing agents, (3) enzyme inhibitors, (4) digestive additives, (5) disinfectants, (6) masking agents and counteractants, and (7) adsorbents.

Smith et al. (2004) investigated the use of an aluminum chloride (AlCl_3) solution as a pH modifier. This compound was added to shallow pits in a swine barn for 42 days and was found to be effective in reducing pH and ammonia concentrations. At 0.75% (vol:vol) level of aluminum chloride solution added to manure, pH was decreased from 7.48 to 6.69 and ammonia was reduced by 52%. Though this acidifier was effective in reducing ammonia concentration, it is still uneconomical to use because of the large amounts required to apply in pits. Moreover, the application of acidifiers may favour the formation and consequently the emission of hydrogen sulphide (Shah et al., 2007).

Aside from their capability to oxidize odorous organic materials into less odorous products, oxidizing agents such as hydrogen peroxide and potassium permanganate could also destroy odour-producing bacteria which are responsible for the formation of hydrogen sulphide and ammonia (Shah et al., 2007). In a study conducted by Govere et al. (2005), calcium peroxide and hydrogen peroxide, used singly or in combination with minced horseradish roots, were found effective in reducing odour. Williams and Schiffman (1996) also reported that potassium permanganate reduced odour intensity and improved odour quality of hog waste. However, these oxidizers break down rapidly and are corrosive in nature (Shah et al., 2007).

Inhibitors with enzyme urease could restrain the conversion of urea from animal urine to ammonia (Shah et al., 2007). However, limited studies have been done on the use of these additives in mitigating gas emissions because of economic issues and the need for frequent application to hog waste to achieve significant improvements (McCrory and Hobbs, 2001).

By breaking down odorous compounds in the manure, digestive additives which may contain a mixture of enzymes and/or bacteria could solve the long-term problem of air quality in

pig houses and lagoons (Shah et al., 2007). Chastain (2000) studied the addition of Bio-Safe (a proprietary name of an additive containing enzymes and microbes) to the effluent at 0, 67, 100 and 200 ppm. Results showed that the addition of the product at a concentration of 100 ppm led to a 36% odour reduction. Hendriks et al. (1997) added 4.5 kg of a mixture of enzymes, bacteria, yeast and mold to a deep pit for 22 months and over four measurement periods, an average reduction of 30% on ammonia emission was achieved. Another additive, Bio-Kat, was sprayed to a lagoon and to five barn pits at varying concentrations (Schneegurt et al., 2005). Results showed that ammonia levels in barns and treatment lagoons decreased significantly with increased application rate. However, not all digestive additives succeed in improving air quality. In a study by Williams and Schiffman (1996), a digestive deodorant with microorganisms and enzymes was found to be ineffective in treating waste from pig barns. Thus, the effectiveness of digestive additives is dependent on the types of enzymes or bacteria present and their use is limited to a reduction of specific compounds (Shah et al., 2007).

Disinfectants can reduce odour and gas emissions through their antimicrobial effects. Varel (2002) reported that 2.5 ppm of natural antimicrobials (carvacrol and thymol) were effective in controlling the generation of odorous compounds from fresh manure for 56 days. Hydrogen cyanide, as discussed by McCrory and Hobbs (2001), decreased hydrogen sulphide and odour emissions from pig slurry. Although disinfectants were found to be effective in reducing odour and gas emissions, they are not widely used at the farm scale because of their characteristic to neutralize rapidly which necessitates repeated application (McCrory and Hobbs, 2001).

To date, the efficiency of masking agents and counteractants in reducing odours associated with hog waste has not been thoroughly investigated. Basically, masking agents are

mixture of volatile oils that cover an objectionable odour with a more pleasant one while counteractants neutralize manure odour to lessen the intensity of the perceived odour (ASABE, 2007).

Adsorbents are materials which are used to bind odorous compounds on their surfaces (ASABE, 2007). Zeolite and sphagnum peat moss have been investigated as adsorbents to improve air quality. In a lab-scale experiment conducted by Portejoie et al. (2003), zeolite reduced ammonia emission from pig slurry. Further, they reported that zeolite could reduce ammonia emissions in hog houses if applied to pits, but distributing the bulk material throughout the pits under the slats would be difficult. A similar problem was raised when they evaluated sphagnum peat moss cover although it was found to adsorb ammonia and eliminated the chance of ammonia volatilization. However, William and Schiffman (1996) reported that sphagnum peat moss was ineffective in reducing odours from fresh manure slurry.

2.1.3.3 Oil sprinkling

The oil sprinkling technique has been proven to be effective in reducing dust concentrations in animal buildings. Dust is known to be an odour-carrier, thus by reducing dust levels, odour and gas emissions could be reduced as well. Heber et al. (2004) investigated the abatement of gases (hydrogen sulphide, ammonia and non-methane hydrocarbons), dust concentrations, and odour emissions from swine finishing barns by sprinkling soybean oil or misting essential oils. Results showed that oil sprinkling was able to reduce the dust levels as well as ammonia and odour emissions while misting oils slightly improved the hedonic tone of barn air. In addition, spraying various additives including soybean oil and essential oil (mixture of herb and ravenda) were evaluated by Kim et al. (2008) to reduce the emission of odour,

ammonia and sulfuric compounds from a confined pig facility. Their study revealed that, of all the additives, essential oil achieved the greatest reduction potential for hydrogen sulphide, ammonia and odour generation after 24 hours of application.

However, a contrary result on ammonia emission was reported by several studies. Godbout et al. (2001) reported that canola oil sprinkling in grow-finish chambers significantly reduced dust and odour levels but had no significant effect on hydrogen sulphide and ammonia emissions. Jacobson et al. (1998) also had similar observations regarding the impact of oil sprinkling on ammonia emission when they sprinkled soybean oil inside a nursery facility.

2.1.3.4 Biofiltration

Following the principle of a biological air purification system, biofiltration uses microorganisms capable of breaking down undesirable organic and inorganic components of air and produces simple end products like carbon dioxide and water (Hartung et al., 2001). Biofilter needs a moist surface area as large as possible to boost the activity of microorganisms in decomposing offensive odours (Hartung et al., 2001). It is typically composed of a reactor packed with a matrix of biological residues such as compost, peat and soil, and bulking agents which include heather, wood chips, and synthetic material (Nicolai and Janni, 2001).

Research on the use of biofilters has been carried out to reduce the emission of odour and gases from hog barns. Martinec et al. (2001) investigated five different biofilter materials (biochips, coconut-peat, a mixture of bark and chopped wood, Bio-Contact filter pellets from compost and bark, as well as compost) on odour reduction potential and overall efficiency. Biochips and the mixture of coconut fibre and fibre peat produced the highest average odour reduction of about 81%. However, all biofilters tested showed minimal reduction in ammonia.

The biofilter study of Hartung et al. (2001) using a 6.5-year old filter bed material achieved an average reduction of 15 to 36% in ammonia and 78 to 80% in odour. The filter bed material was a mixture of coconut and peat fibres with wood batten as the filter screen. In addition, an average reduction of 41, 51, and 83% in ammonia, odour, and hydrogen sulphide, respectively, was reported by Chen et al. (2008) using a western cedar wood chip-based biofilter.

Even with the attainment of significant reduction of hydrogen sulphide, ammonia and odour emissions, still the use of a biofilter system has not been well adopted by swine producers. The main drawbacks of biofilters are their high operating costs in supplying high air flow due to significant pressure drop across the filter media (Riskowski, 2004), and the need to continuously provide a conducive environment for microbes to grow which requires an operator with good technical expertise on the process (Nicolai and Janni, 2001).

2.2 Nanotechnology

Nanoscale science, engineering, and technology, or nanotechnology is the use of materials with a size range from 1 to 100 nanometres (billionths of a metre) in at least one dimension (EPA, 2007). These materials could be nanofilms (one dimension), nanowires and nanotubes (two dimensions), or nanoparticles (three dimensions) (Handy et al., 2008). Nanotechnology is not merely about the small size dimension involved, but more importantly, it is the ability to work with matter at the atomic or molecular scale (Masciangioli and Zhang, 2003). This resulted in materials that exhibit novel properties different from that at macro levels (Masciangioli and Zhang, 2003). Thus, many regard nanomaterials as “tiny objects with huge opportunities” (Boxall et al., 2007).

Nanomaterials, especially nanoparticles, have played an important role in the advancement of nanotechnology. They are seen as having great potential in various fields of research and applications. Recently, manufactured nanoparticles are used in electronics, biomedicine, pharmaceuticals, cosmetics, environmental analysis and remediation, waste and water treatments, catalysis and material sciences (Ju-Nam and Lead, 2008; Tiede et al., 2009).

2.2.1 Properties and characteristics of nanoparticles

In any media, the physical and chemical properties associated with nanostructured materials deviate significantly from their bulk counterparts (Okuyama et al., 2006; SCENIHR, 2006). These unique characteristics give them novel features that are highly desirable for a variety of commercial applications (EPA, 2007). Among the quantum properties, research has indicated that size and physical structure, and surface chemistry of nanomaterials are the vital ones in determining their biological, chemical and physical responses (Donaldson et al., 2000; Oberdorster, 2000; Brown et al., 2001; Sellers, 2009).

One of the valuable attributes of nanoparticles is their very small size which translates to a very high surface area to volume ratio and consequently more sites for surface reaction (Li et al., 2006; Ju-Nam and Lead, 2008). With this characteristic, nanoparticles can promote degradation of contaminants in air, soil and water, and thus, make them highly flexible for *in situ* remedial applications (Montas and Shirmohammadi, 2004). However, due to their minute size, the solubility of nanoparticles increases and could allow them to easily traverse cells and cellular membranes. Attachment of these particles to the organelles can impair cellular functions and might cause fatal effects (Maynard and Kuempel, 2005).

Interactions between materials due to weak intermolecular forces such as Van der Waals forces can cause nanomaterials to agglomerate and form larger structures (Sellers, 2009). As a result, their concentration will decrease rapidly, and their size-dependent characteristics and behavior will be altered (Kandlikar et al., 2007), thereby decreasing their application efficiency. Additionally, this agglomeration between nanomaterials significantly determines their fate and extent of distribution to the environment (SCENIHR, 2006).

2.2.2 Applications of nanoparticles in environmental remediation

Due to their unique physical, chemical and biological properties, nanoparticles have been increasingly gaining interest in the area of environmental engineering with emphasis on pollution prevention, treatment and remediation. Most of these nanoparticles have been directly applied to contaminated media or used as reactive agents in filtration systems.

2.2.2.1 Ground and wastewater treatments

In a study conducted by Hu et al. (2005), synthesized nanoscale maghemite particles were evaluated for use in the removal and recovery of hexavalent chromium Cr(VI) from wastewater. Maghemite nanoparticles as adsorbents of hexavalent chromium reached equilibrium within 15 min and were independent of initial chromium concentration. Their adsorption capacity was selective and more favourable to Cr(VI) compared with other adsorbents such as activated carbon and clay. In addition, the nanoparticles still retained the original metal removal capacity although they underwent six successive adsorption–desorption processes.

Nanoparticles have also been used in the remediation of agricultural lands and groundwater contaminated by farm run-off. Bimetallic particles (Fe/Pd) of 100 to 200 nm size

were evaluated by Elliot and Zhang (2001) as a remedial technique for groundwater contamination due to trichloroethene (TCE). In this study, about 1.3 g/L of nanoparticle suspension (1.7 kg of Fe/Pd nanoparticles) was gravity-fed into an injection well located in a facility with a well-characterized groundwater quality. Within 2 days after nanoparticle application, a considerable reduction of trichloroethene concentration was observed, reaching up to 96% over the 4-week monitoring period. Another study was performed by Varadhi et al. (2005) using a full-scale nanoiron injection to treat groundwater contaminated with chlorinated hydrocarbons. The nanoiron slurry was applied in a 6.1-metre injection grid pattern at a concentration of up to 30 g/L. During the post-injection monitoring, results showed 90% reduction in the dissolved chlorinated contaminant concentration at various locations within the treatment area. Tungittiplakorn et al. (2004) explored the use of engineered amphiphilic polyurethane (APU) nanoparticles in removing phenanthrene (PHEN) from a sandy aquifer material. The 17 to 97 nm colloidal particles were made of polyurethane acrylate anionomer (UAA) or poly (ethylene glycol)-modified urethane acrylate (PMUA) precursor chains. Due to their hydrophilic surfaces, PMUA nanoparticles were found to be more mobile in soil and thus, had a faster rate of PHEN removal than water alone.

2.2.2.2 Water and air purification

The performance of silver nanoparticles coated onto polyurethane (PU) foams as an antibacterial water filter was assessed by Jain and Pradeep (2005). Results showed that no bacterium was detected downstream when the input water with a bacterial load of 1×10^5 to 1×10^6 CFU/mL passed through the filter. Thus, their experiments suggested the possibility of the use of this material in air quality management, water and air purification systems, antibacterial packaging, among other things.

Lee et al. (2005) used a solid montmorillonite (MMT) and an *in situ* generated agglomerated silica for capture of cadmium oxide which have been found to be the predominant compound in combustion environment. Of the two nanostructured sorbents, the nanostructured silica agglomerates were more stable and valuable than the montmorillonite sorbent. This can be attributed to its high surface area, and its greater effectiveness in chemisorption and suppressing nucleation of cadmium species.

Another application of nanoparticles is the use of titanium dioxide (TiO₂) photocatalyst for air purification. Nonami et al. (2004) developed an apatite-coated titanium dioxide photocatalyst by soaking the titanium dioxide powder in a solution containing phosphate ions for 1 hr at 37°C. Results showed that the newly prepared composite material can be applied as an antibacterial and environmental purification material due to its ability to adsorb and putrefy bacteria and various organic matters. Another titanium dioxide photocatalyst filter was prepared by Kim et al. (2006) using sol-gel method. The technique involved mixing 100 g of titanium isopropoxide with 20 g of anhydrous ethanol, and the resulting solution was heated up to 80°C for more than 6 hours. Due to larger surface area and higher titanium dioxide content of the photocatalyst, the air-purifying device has been proven to be effective for germ-sterilization and decomposition of hazardous organic materials.

2.2.3 Potential use of nanoparticles in swine industry

Asis (2008) evaluated the potential application of nanoparticles for the reduction of gas and odour emissions from swine manure slurry. Of the twenty-four commercially-available nanoparticles identified as having been used in environmental remediation, twelve were selected based on their previous similar applications, properties (toxicity, flammability, stability and

reactivity) and cost. These include aluminum oxide (Al_2O_3), magnesium oxide (MgO), calcium oxide (CaO), aluminum oxide plus (Al_2O_3+), magnesium oxide plus ($\text{MgO}+$), titanium dioxide (TiO_2), zinc oxide (ZnO), lanthanum oxide (LaO), manganese oxide (MnO), calcium oxide plus ($\text{CaO}+$), iron oxide (Fe_3O_4) and tungsten oxide (WO_3).

The effectiveness of the twelve nanoparticles in reducing hydrogen sulphide, ammonia and odour levels was evaluated in a fully-controlled small scale set-up using three deployment techniques: headspace spraying, mixing with the slurry and headspace gas filtration. Spraying was done by dispersing the nanoparticles into the headspace of the manure slurry using an air compressor. Mixing method involved direct incorporation of the nanoscale powder into the slurry. Headspace gas filtration was conducted using a sampling set-up where manure gases were passed through a filter cassette assembly loaded with nanoparticles.

For each deployment method, Asis (2008) conducted a series of tests involving the twelve nanoparticles to establish the sampling parameters and to identify the nanoparticle that exhibited the highest reduction on odour, hydrogen sulphide and ammonia emissions. Results from these tests revealed that the most promising nanoparticle in headspace spraying technique was tungsten oxide while zinc oxide nanoparticles was identified as the most effective material for both mixing and gas filtration methods (Asis, 2008). The most effective nanoparticle in each deployment technique was further investigated to optimize the experimental factors such as application rate, air flow rate, contact period as well as particle dispersion pressure, and to determine its potential in reducing gas and odour levels. Table 2.4 outlines the experimental parameters measured and the results of the optimization test.

Table 2.4. Summary of the optimization tests conducted by Asis (2008) for each deployment technique.

Experimental Parameters and Results	Headspace Spraying	Mixing with the Slurry	Headspace Gas Filtration
Test parameters			
-- nanoparticle used	tungsten oxide (WO ₃)	zinc oxide (ZnO)	zinc oxide (ZnO)
-- application rate	0.01, 0.025 and 0.05 g/L of headspace volume and applied at 414 kPa (60 psi)	0.1, 0.25, and 1.5 g/L of manure slurry	1.5, 3 and 6 g of nanoparticles loaded into the 37-millimetre filter assembly; manure gas flow rate of 500 mL/min
-- test media	120-litre containers with 30 L of manure	120-litre containers with 30 L of manure	50 L manure gas
Results	<p>1. No significant reduction on the levels of hydrogen sulphide, ammonia and odour</p> <p>2. No significant effect on manure properties and characteristics</p>	<p>1. At a rate of 1.5 g/L, hydrogen sulphide concentration was reduced by 98% while ammonia levels was increased by 129%</p> <p>2. Significantly reduced odour concentration but not the hedonic tone</p> <p>3. Slight increased in pH and concentration of Zn in the manure</p>	<p>1. Filter bed with 6 g of zinc oxide was able to reduce hydrogen sulphide by 89%, ammonia by 86% and odour concentration by 74%</p> <p>2. Effect of pressure drop on flow rate and loading amounts was not evident</p>

Spraying of tungsten oxide nanoparticles into the headspace of the slurry did not result to considerable reduction on hydrogen sulphide, ammonia and odour concentrations. Incorporating zinc oxide nanoparticles into the manure slurry at a rate of 1.5 g/L reduced the concentrations of hydrogen sulphide and odour. However, the concentration of ammonia increased as the particle-to-slurry ratio was increased. This trend was opposite to that in the filtration method wherein the

packed bed filter with zinc oxide nanoparticles significantly reduced ammonia levels by 86%. In addition, a filter bed with 6 g of zinc oxide was able to reduce hydrogen sulphide by 89% and odour concentration by 74%. Thus, among the three deployment methods, direct mixing with the slurry and filtration of manure gas using zinc oxide nanoparticles showed promising results in reducing the levels of gas and odour emitted from swine manure (Asis, 2008).

2.3 Summary

Emissions of hydrogen sulphide, ammonia and odour from swine production operations are largely produced from fresh or stored manure. These emissions have been a long-term concern to humans, animals and the environment despite several abatement strategies that have been investigated and adopted at the farm scale. With the advent of nanotechnology, Asis (2008) evaluated the use of nanoparticles and results revealed that filtration and mixing methods using zinc oxide nanoparticles showed great potential in controlling hydrogen sulphide, ammonia and odour emissions from swine manure.

One possible application of filtration method is the installation of a filter system loaded with nanoparticles either in recirculation or exhaust ducts. On the other hand, the method of incorporating nanoparticles into the slurry could be applied during pit-plug pulling, pit cleaning and other manure handling activities in the barn. With the investigation of the effectiveness and feasibility of nanoparticles in treating environmental pollutants from swine barns in room-scale set up, a new abatement strategy that is effective will be formulated. Moreover, results of this study could also serve as a starting point for exploring the use of other nanomaterials and other possible deployment techniques.

3 KNOWLEDGE GAPS AND OBJECTIVES

Despite several studies conducted on possible gas mitigation techniques, the environmental and occupational issues associated with the emissions of hydrogen sulphide, ammonia and odour from livestock facilities still remain unresolved. Recognizing the recent advances in nanotechnology, Asis (2008) has evaluated the potential application of nanoparticles in treating gases emitted from swine manure. Using a fully-controlled small-scale test set-up, mixing and filtration methods with zinc oxide (ZnO) nanoparticles showed significant results in reducing the levels of gases and odour from manure slurry. However, there is a gap of translating these results to commercial swine production conditions. Nanoparticles and manure gases can react and behave differently under different conditions, thus further investigation of the effectiveness of zinc oxide nanoparticles in an environment that closely represents actual barn conditions is needed. Additionally, the most effective application rate (particle-to-slurry ratio for mixing method and loading amount for filtration method), the effects of nanoparticle addition on the treated manure, and the effects of filter design and face velocity on the performance of filters with zinc oxide nanoparticles can be appropriately evaluated in a larger-scale open system test. Room scale experiments under conditions close to a normal production setting would provide the opportunity to test the effectiveness and economic feasibility of this technology in real livestock operations.

The overall goal of this study was to control the emissions of hydrogen sulphide, ammonia and odour from swine barns using zinc oxide nanoparticles applied through mixing and gas filtration methods. Specifically, this research work was conducted to:

1. evaluate operational factors including nanoparticle application rate, filter design, and face velocity that affect the effectiveness of zinc oxide nanoparticles in semi-pilot scale open systems;
2. determine the effectiveness of zinc oxide nanoparticles in reducing hydrogen sulphide, ammonia and odour emissions in room-scale tests simulating commercial swine production conditions;
3. assess the impact of the treatment on manure characteristics and hog performance; and
4. determine the economic viability of using zinc oxide nanoparticles to control the levels of hydrogen sulphide, ammonia and odour in swine barns.

4 MATERIALS AND METHODS

The effectiveness of mixing and gas filtration methods with zinc oxide nanoparticles as possible measures to control the emissions of hydrogen sulphide, ammonia and odour from swine barns was evaluated in this study. Mixing involved the incorporation of zinc oxide nanoparticles into the manure to inhibit the production of gases while gas filtration method involved the installation of a filter with zinc oxide nanoparticles to control the airborne levels of gases from manure. The zinc oxide nanoparticles used in each test were acquired from NanoScale Corporation in Kansas, USA. The distinct characteristic of zinc oxide nanoparticles compared with their bulk counterparts is their higher surface area to mass ratio as a result of their very small size. From the data provided by the manufacturer, zinc oxide nanoparticles had a crystallite size of about 10 nm and an estimated specific surface area of 70 m²/g. These unique features would result to increased sites for physical, chemical and biological reactions (Li et al., 2006; Ju-Nam and Lead, 2008).

4.1 General Experimental Plan

The overall approach of this study was to conduct a comprehensive evaluation of mixing and gas filtration methods with zinc oxide nanoparticles in a series of tests that were carried out in a large-scale open system environment (Figure 4.1). Semi-pilot scale tests were conducted to evaluate specific experimental factors such as application rate, filter design and face velocity that affect the effectiveness of the gas mitigation methods. The most effective treatment combination

from each deployment technique was then evaluated in the room-scale tests. These tests were conducted in specially designed chambers simulating actual production conditions to investigate the effectiveness of the treatments in a farm scale. A preliminary cost analysis was then carried out based on the results of both tests to assess the feasibility of the application of ZnO nanoparticles in a typical swine barn.

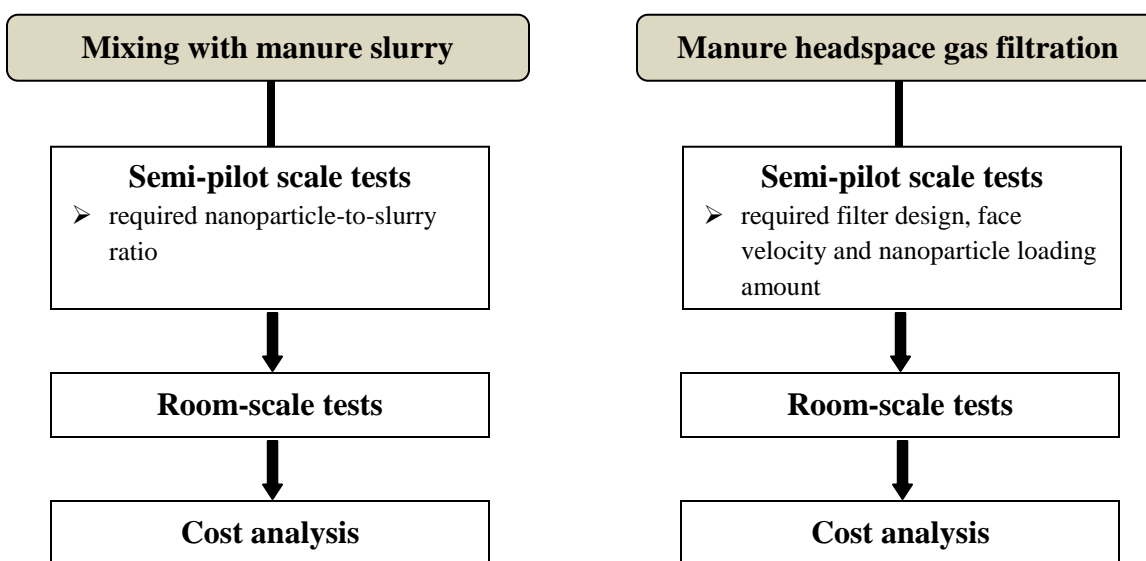


Figure 4.1. Experimental plan for each deployment technique.

4.2 Semi-pilot Scale Tests

4.2.1 Mixing with manure slurry

This test was aimed to assess the effectiveness of incorporating zinc oxide nanoparticles into the manure at various amounts and consequently, to determine the particle-to-slurry ratio required to achieve maximum reduction of hydrogen sulphide and ammonia emissions in an open system. The experiment was conducted in 65-litre open top containers filled with 50 L of manure. Results from the initial test conducted in open system set-up showed that the highest

application rate (1.5 g/L) used by Asis (2008) exhibited only a slight reduction in hydrogen sulphide level. Thus, the particle-to-slurry ratios tested in this experiment were increased to 1.5, 3, 6 and 8 grams per litre of slurry in an attempt to obtain a greater reduction in gas concentration. One container was designated as a Control and did not receive any treatment. Three replicate trials were done; each trial lasted for 20 days.

Test Materials and Experimental Set-up

Five 65-litre open top containers (experimental totes) were placed in a fully-controlled environmental chamber at the barn facility of Prairie Swine Centre Inc. (PSCI) in Saskatoon, Saskatchewan, Canada. Prior to the start of each test, the totes were cleaned, disinfected and dried thoroughly.

Manure samples at about 3 weeks old were collected from one manure pit of a grow-finish room at PSCI using a submersible vacuum pump (Model WS-BHS, Goulds Pumps, ITT Corp., New York, USA). To minimize the effect of manure variation, the area of the pit where the manure samples were taken was mixed thoroughly prior to sample collection. The collected manure slurry was then placed in a 1400-litre open cylindrical tub and mixed again before finally transferred to individual experimental totes. Each tote was filled with 50 L of manure slurry; two 0.4-centimetre diameter polyethylene tubing sampling lines were installed near the center of the tote (Figure 4.2). The inlet to each sampling line had a plastic funnel which was placed at 5 cm above the manure surface as suggested by Jacobson et al. (1997) to capture the gases emitted from the manure.

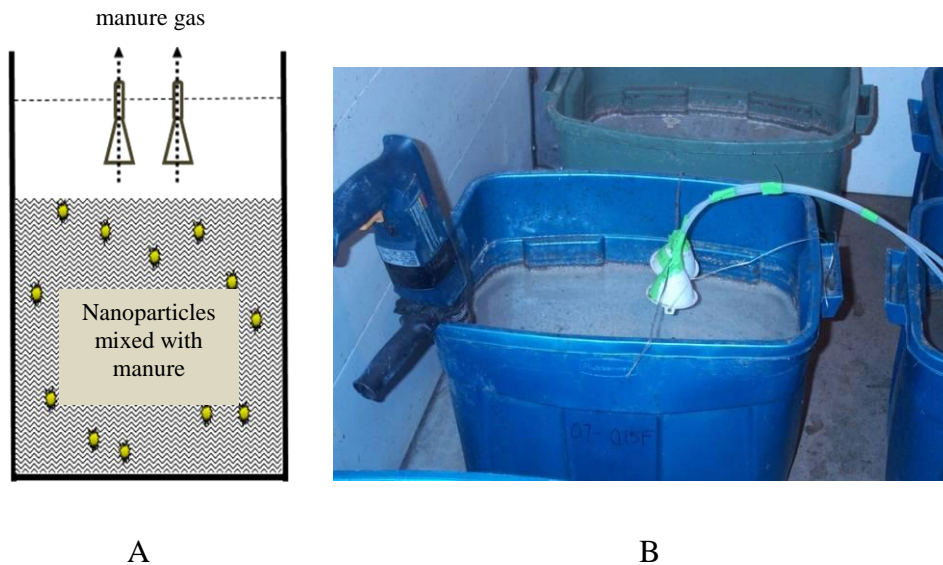


Figure 4.2. Schematic diagram (A) and photo (B) of the set-up used in semi-pilot scale open system experiments for the mixing method.

Experimental Procedure

Manure samples in individual totes were left undisturbed until the first sampling event (Day 5 of the trial). The concentration of gases generated from each container on Day 5 served as baseline data for subsequent sampling events (Days 10, 15 and 20 of the trial). Zinc oxide nanoparticles (treatment) were incorporated into the slurry using a portable mixer after the first gas sampling. Thus, gas sampling done on Days 10, 15 and 20 of each trial corresponded to Days 5, 10 and 15 after the treatment has been applied. During sampling, the manure slurry was mechanically agitated using a mixer. Two representative headspace gas samples were extracted from the sampling lines at 2 minutes from the start of agitation by means of the gas sampling apparatus shown in Figure 4.3. The apparatus was composed of an air tight plastic container with five sampling ports on its transparent cover. The center port was used for a line connected to the

peristaltic pump (Master flex L/S tubing pump, Model 7017-52 pump head, Cole-Parmer, Vernon Hills, USA) while the other four were used for the sampling lines. In this case, however, only two ports were connected to the sampling lines placed near the manure surface, thus leaving the other 2 ports closed and unused. The pump created negative pressure inside the container thereby drawing in air from the sampling lines into the 10-litre Tedlar bags (SKC Inc., Eighty Four, PA, USA). Gas samples in Tedlar bags were analyzed for hydrogen sulphide and ammonia concentrations. In addition, manure pH was measured *in situ* using a digital portable pH meter (Orion 250A, Thermo Scientific, Beverly, MA, USA; accuracy of ± 0.02) after every sampling.

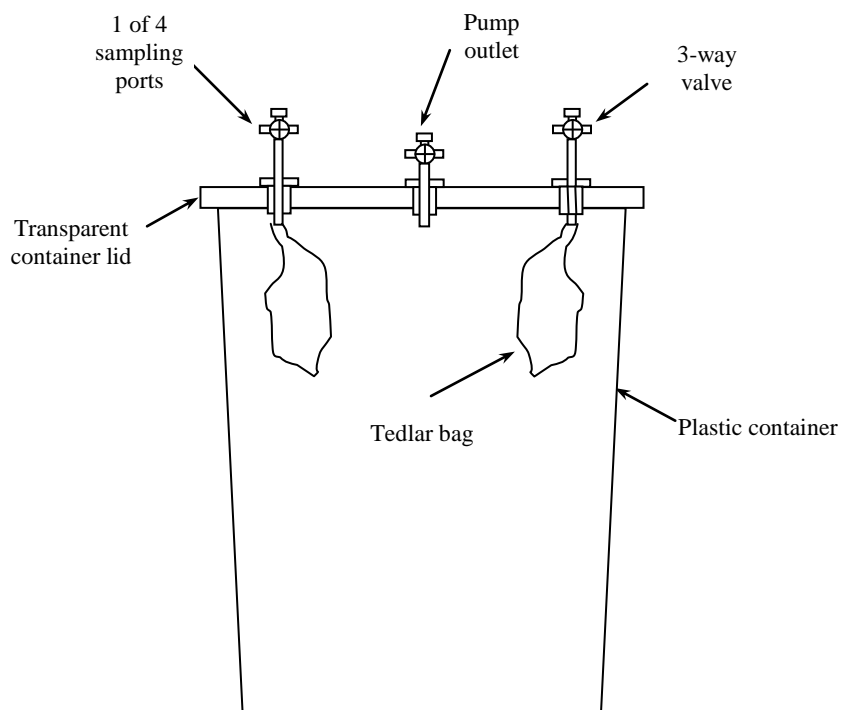


Figure 4.3. Schematic diagram of the gas sampling apparatus.

4.2.2 Manure headspace gas filtration

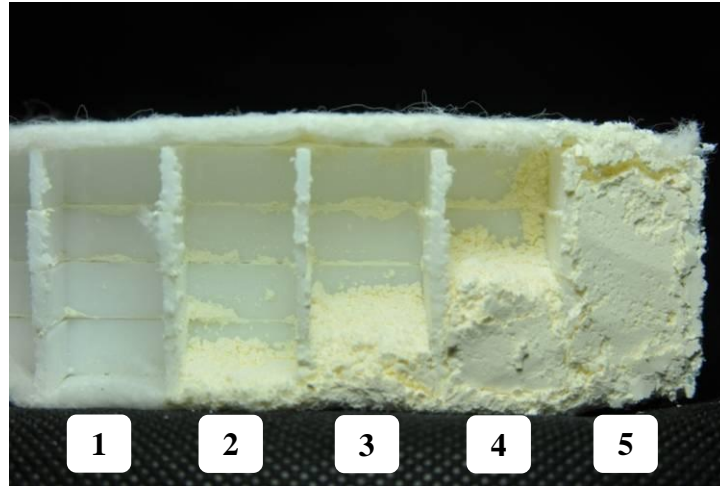
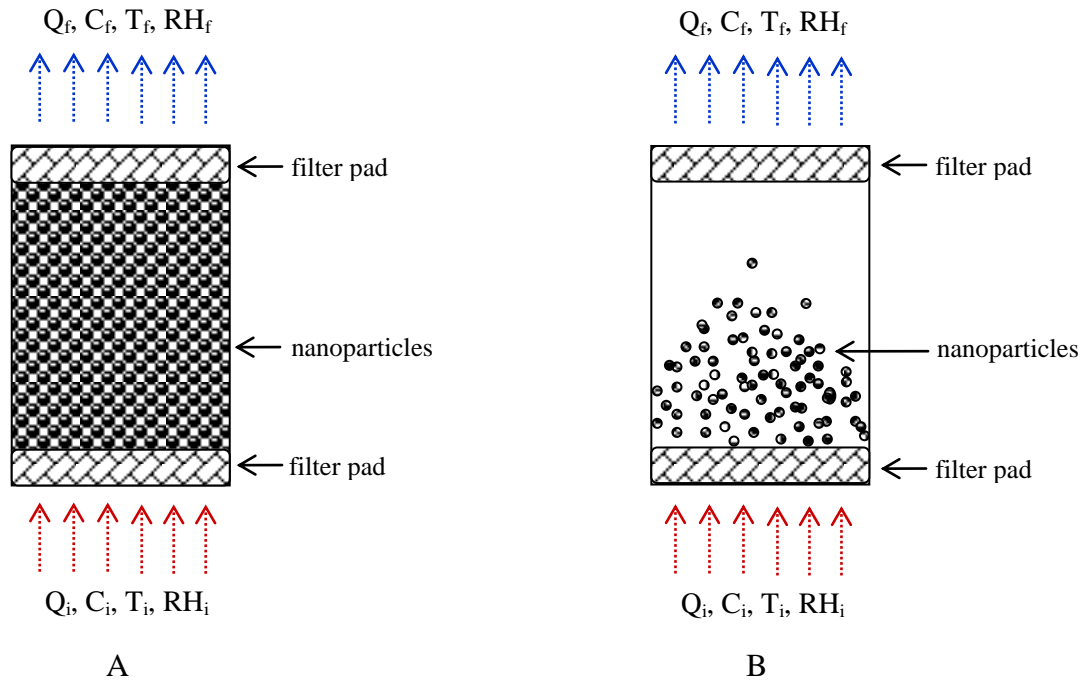
This experiment was conducted to evaluate the effectiveness of two filter designs: packed bed and fluidized bed at various loading amounts and face velocities under conditions close to normal production operations. Packed bed and fluidized bed designs have already been used in bioreactors for bioremediation of an air pollutant (Clarke et al., 2007). For the fluidized bed design, the filters were loaded with 15, 30, and 60 g of ZnO nanoparticles based on the application rates used by Asis (2008), i.e., 0.14, 0.28 and 0.56 g/cm² of filter cross-sectional area. For the packed bed design, these loading amounts were adjusted to 30, 60, and 90 g to form compact bed filters. In addition, a filter pad only (no zinc oxide nanoparticles) was included to serve as a Control. Each filter was subjected to three face velocities of 0.2, 0.5, and 0.8 m/s corresponding to volumetric flow rates of 100, 250 and 400 L/min. Due to a number of operational factors measured including filter design, nanoparticle loading amounts and face velocities, the test was divided into 2 phases. Phase 1 was conducted to determine the most effective filter design and face velocity. The most effective combination was then used in phase 2 tests to determine the loading amount required to achieve a significant reduction in hydrogen sulphide and ammonia levels. Three replicates of both phases were conducted.

Test Materials and Experimental Set-up

Figure 4.4 shows the schematic diagram of the packed bed and fluidized bed filter designs. In the packed bed filter, nanoparticles were fully compacted into the filter housing (Figure 4.4-A). In the fluidized bed filter design, the filter housing was not completely filled with nanoparticles, thus leaving extra air space to allow “fluid-like” behavior of the particle-air mixture when the airstream was passed through the filter (Figure 4.4-B). The filter media of both designs had a cross-sectional dimension of 11.4 cm (L) x 10.2 cm (W). The thickness of the

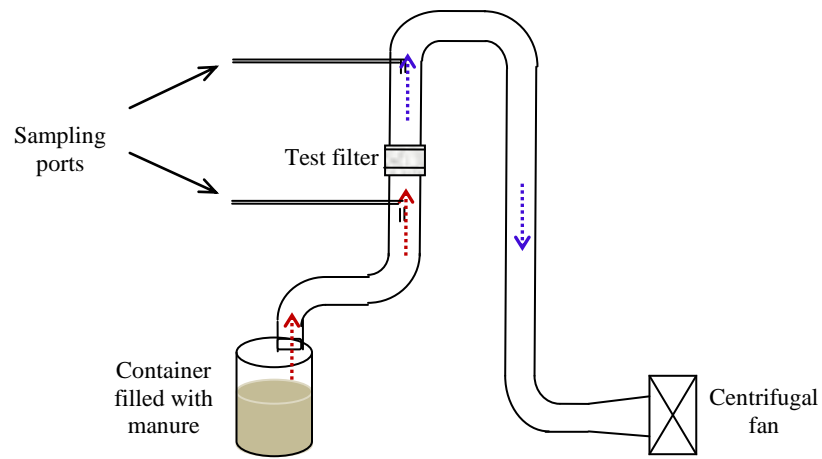
packed bed filter housing was dependent on the loading amount of nanoparticles while that in the fluidized bed was constant at 3.2 cm regardless of the amount of nanoparticles. Actual depth of nanoparticles in fluidized beds was about 0.4, 0.8 and 1.6 cm for 15, 30 and 60 g loading amounts, respectively. For both designs, the filter housing was made of a plastic styrene with honeycomb structure of 1.5 cm x 1.5 cm openings to ensure uniform distribution of the nanoparticles across the filter area. Both sides (upstream and downstream) of the plastic structure were covered with a commercially-available filter pad material (Model HPE30621 Electrostatic Hammock filter pad, True Blue Company, LaPorte, Indiana, USA) to hold the nanoparticles within the filter.

As shown in Figure 4.5, the test set-up was operated on a negative pressure relative to the surrounding space. Air movement in the duct was achieved by installing a centrifugal fan (Model Keho, Edwards Group, Lethbridge, AB) that extracted gases from the headspace of a 75-litre plastic bucket filled with 30 L of manure and passed through a 10-centimetre diameter galvanized sheet metal duct where the test filter was installed. Fan speed was controlled using an adjustable speed alternating current (AC) inverter (Leeson Speedmaster, Mississauga, ON) and monitored using an anemometer (Model 8330 VelociCheck, TSI Incorporated, St. Paul, MN; accuracy of $\pm 5\%$ of reading) in order to ensure a constant gas velocity throughout the experiment. To ensure that significant levels of challenge gas were passed through the test filter, the manure in the plastic buckets was continuously agitated using a mechanical mixer. Two sampling ports were installed on the duct, one at the upstream and another one at the downstream side of the test filter to monitor the levels of gases before and after filtration.

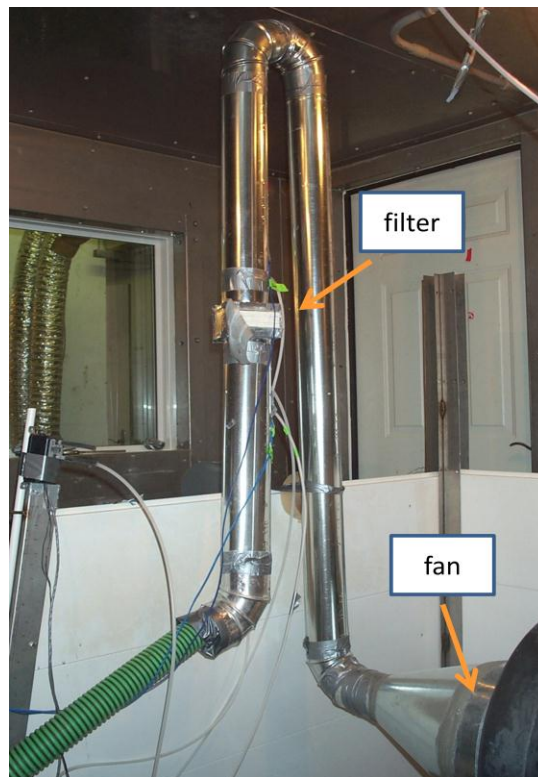


C

Figure 4.4. Schematic diagrams of packed bed (A) and fluidized bed (B) filters during filtration, and a photo of the cross-section of the test filters (C). Each compartment in the photo represented the sample cross-section of a filter pad only (1), fluidized bed filter with 15 g of ZnO (2), fluidized bed filter with 30 g of ZnO (3), fluidized bed filter with 60 g of ZnO (4), and a packed bed filter with ZnO (5). Q , C , T and RH are face velocity (flow rate), gas concentration, air temperature and relative humidity, respectively.



A



B

Figure 4.5. Schematic diagram (A) and photo (B) of the set-up used in semi-pilot scale tests for the filtration method.

Experimental Procedure

Prior to the start of each test, the fan was set to a desired speed and the test filter was then placed in the filter rack. The air velocity before the filter was rechecked and adjusted to the required speed when necessary. The manure in the plastic bucket was pre-agitated for 2 minutes to generate measurable levels of target gases to be introduced to the filter. These manure samples were about 3 weeks old and were taken from one of the underfloor pits in a grow-finish room at PSCI.

For phase 1, only 1 bucket was used as a source of manure gas. A constant volume (500 L) of gas was passed through the filter media regardless of face velocity. This was achieved by varying the length of time of filter exposure. For 0.2 m/s (100 L/min), gas samples were withdrawn from the sampling ports using the gas sampling device described in Figure 4.3 after 5 min of filter exposure to manure gases while 2 and 1.25 min for face velocities of 0.5 m/s (250 L/min) and 0.8 m/s (400 L/min), respectively. For phase 2, with constant flow rate (face velocity) used, manure gas was passed through each test filter over an extended period of 30 min. To maintain the levels of hydrogen sulphide and ammonia in the gas stream being passed through the filter, 6 manure buckets were used consecutively as gas sources, with each bucket agitated continuously for 5 min during the process. Gas samples were extracted through the upstream and downstream sampling ports at 1, 3, 5, 10, 15, 20, 25 and 30 min from the start of gas exposure and passed through gas analyzers to determine the concentrations of hydrogen sulphide and ammonia before and after filtration.

In addition, air temperature and relative humidity at the upstream and downstream side of the filter were also monitored using temperature-humidity sensors (Hobo U12-013, Onset

Computer Corp., MA, USA; accuracy of $\pm 2.5\%$). Pressure drop across the filter assembly was measured using a pressure transducer (Model 264, Setra Systems, Inc., Boxborough, MA; accuracy of ± 6 Pa).

4.3 Room-scale Tests

4.3.1 Mixing with manure slurry

Using the most effective particle-to-slurry ratio determined in the semi-pilot scale tests, the effectiveness of mixing zinc oxide nanoparticles into the slurry was evaluated in a room-scale test under actual barn conditions. The experiment was conducted in two specifically designed chambers at the PSCI barn facility. One chamber was configured as a normal swine room (Control) with no treatment applied while the manure slurry in the other chamber was treated with zinc oxide nanoparticles (Treatment).

Test rooms and animals

Two identical and fully instrumented environmental chambers at the PSCI barn facility were used in this test. Each chamber had inside dimensions of 4.2 m (L) x 3.6 m (W) x 2.7 m (H) with ceiling and internal walls covered with stainless steel sheets to eliminate emissions from these surfaces. Both chambers housed an equal sized pen with partially slatted concrete flooring within the pen area (Figure 4.6). The pen had a commercial feeder and cup-type water drinker, and was surrounded with plastic matrix flooring for easy access to the collection tub underneath the slatted floor. The tubs in the two chambers were almost identical in size with dimensions of approximately 2 m (L) x 1.25 m (W) x 0.3 m (H) and had a capacity of approximately 900 L. Before the start of each experiment, both chambers were cleaned and disinfected thoroughly. The feeders and manure collection tubs were emptied and washed.

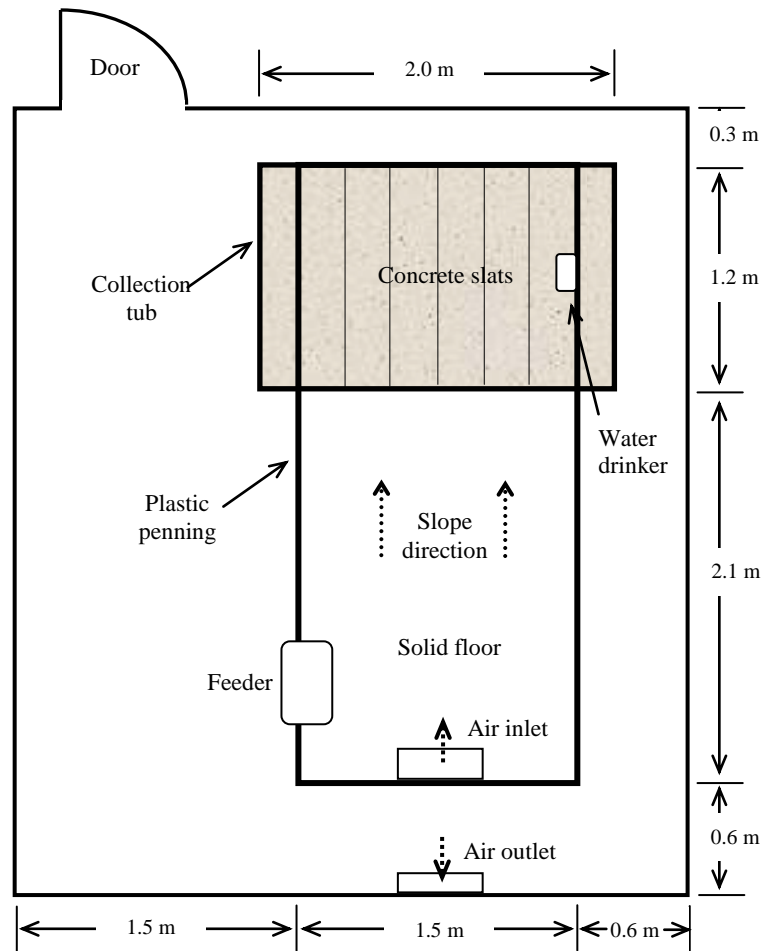


Figure 4.6. Layout of one of the environmental chambers used in room-scale experiments for the mixing method; the second chamber was identical to this chamber.

The two chambers and the adjacent instrumentation room were located inside one big airspace operated on a negative pressure ventilation system. Fresh air entered into this airspace through ceiling inlets and was conditioned at desired settings using a 5-ton air conditioning unit (Raka-060 CAZ, Setra Systems, Boxborough, MA, USA) or a 10-kilowatt electric heater (Chromalox, Dimplex North America Ltd., Cambridge, ON, Canada). The pre-conditioned room air was passed through a filtration unit (Circul-Aire USA-H204-B, Dectron International,

Roswell, GA, USA) with a 0.6-metre diameter centrifugal fan (Delhi BIDI-20, Delhi Industries Inc., Delhi, ON, Canada) and entered the chambers through an actuated inlet located on the ceiling of each chamber. An additional 2-kilowatt in-duct heater was installed in the supply duct of each chamber to add heat when necessary. Air from the chamber was exhausted through one sidewall fan (H18, Del-Air Systems Inc., Humboldt, SK, Canada). Except for the air conditioning unit, all equipment were controlled with a Rapid Control System (Del-Air Systems Inc., Humboldt, SK, Canada). Sensors and other monitoring instruments were deployed in each room, and were calibrated and checked to ensure proper operation during the course of the test.

Eight female grower pigs of about 28 to 30 kg were housed in each pen within the chamber. The animals were weighed and sorted at the start of each trial such that the average initial weights in both rooms were within ± 1 kg of each other. Standard grow-finish diets (from Starter 3 to Grower 2 feed) were provided to pigs during the course of the trials and were always weighed before putting into the feeders. The formulations and basic analysis of the diets are shown in Table A.1 (Appendix A). In addition, daily checks were done to monitor the health status of the animals.

Experimental Procedure

This test was carried out in three replicate trials, each lasted for 30 days. At the start of each trial, the dunging-laying pattern of the animals was established by wetting the dunging area (slatted floor) with water and spreading feed on the laying area (solid floor). The first 15 days of the trial served as the manure accumulation period. First gas sampling was done on Day 15 of the trial to determine the initial gas concentration in each chamber. Immediately after the first sampling, zinc oxide nanoparticles at a rate of 3 g/L were applied to the manure slurry collected

in the manure tub under the slats in one of the chambers (Treated). Treatment application was done by incorporating the nanoparticles into a plastic bucket filled with 30 L of manure taken from the collection tub of the same chamber. The nanoparticle-manure mixture was then applied into the manure in the tub and mixed with the bulk of the slurry using a steel rake which was gently pulled over the entire length of the tub four times. Subsequent sampling events were done on Days 20, 25 and 30 which corresponded to Days 5, 10 and 15 after treatment application.

To monitor the concentrations of ammonia, hydrogen sulphide and odour in the two chambers and to assess their spatial variation within the chamber air space, sampling lines were placed at three specific locations in each chamber (Figure 4.7): at the pit (approximately 5 cm above manure surface), at pig's height (approximately 0.5 m above the pen floor) and at human level (approximately 1.6 m above the floor). During sampling, manure slurry in the tub was agitated using a steel rake and a recirculating vacuum pump to simulate the handling of the slurry during periodic clearing of manure deposited in underfloor pits in normal swine production rooms. The agitators were operated simultaneously and continuously for 5 minutes. Air samples were withdrawn through the sampling lines at 2, 5 and 10 minutes from the start of agitation and collected in 10-litre Tedlar bags using the gas sampling apparatus shown in Figure 4.3. Prior to gas collection, the Tedlar bags and sampling lines were purged with clean air (zero gas) twice (Praxair, Saskatoon). Pigs were moved to an adjacent room during sampling and were returned to the room after sufficient ventilation was achieved.



Figure 4.7. Air sampling points in each chamber: pit, animal and human levels.

Aside from measuring odour and target gases, the effects of the treatment on manure characteristics and pig performance such as average daily gain and feed intake, manure production rate as well as water usage, were also assessed. Table 4.1 summarizes how each parameter was monitored.

The management of the two chambers was kept as identical as possible throughout the test and in accordance with conventional husbandry practices in the normal production rooms. Air temperature was initially set at 21°C and then gradually decreased to 18°C at Week 4 following standard temperature guidelines for grower pigs (PSCI, 2000). Indoor air quality (temperature, relative humidity and ventilation rate) in each chamber was regularly monitored to ensure that both rooms had the same environmental conditions. Type-T thermocouples were

installed at the inlet and at the middle of the chamber for monitoring temperatures. Relative humidity was measured using humidity sensors (Hobo U12-013, Onset Computer Corp., MA, USA; accuracy of $\pm 2.5\%$) situated in the middle of the room. Ventilation rate was determined through an iris damper (Continental Fan Manufacturing, Buffalo, N.Y., USA; accuracy of $\pm 5\%$) installed at the exhaust duct of each chamber. The pressure difference across the damper was measured using a pressure transducer (Model 264, Setra Systems, Inc., Boxborough, MA; accuracy of ± 6 Pa). Readings from these monitoring instruments except Hobo sensors were logged using a datalogger (CR1000, Campbell Scientific, Logan Utah, USA). Temperature, humidity and ventilation rate in each chamber were monitored every 10 minutes.

Table 4.1. List of additional parameters monitored during each room-scale trial.

Parameters	Instrument / Analysis	Data Collection
Water usage	Diaphragm-type water meter (Type SF, ABB Water Meters Inc. Florida, USA; min reading of 1 L) attached to the drinker	Daily readings
Manure production*	Depth of manure accumulated in the tub	Daily using a meter stick
Average daily gain (ADG)	Average growth rates during the test period	Weighing at start and end of trial
Average daily feed intake (ADFI)	Dividing the total weight of feed consumed by the product of number of pigs and number of days on feed	Weighing feed loaded into the feeders
Manure properties	Manure samples sent to a commercial laboratory (ALS Environmental Laboratory, Saskatoon, SK)	End of each trial

* A linear correlation between manure depth and volume was established from previous related experiments.

4.3.2 Manure headspace gas filtration

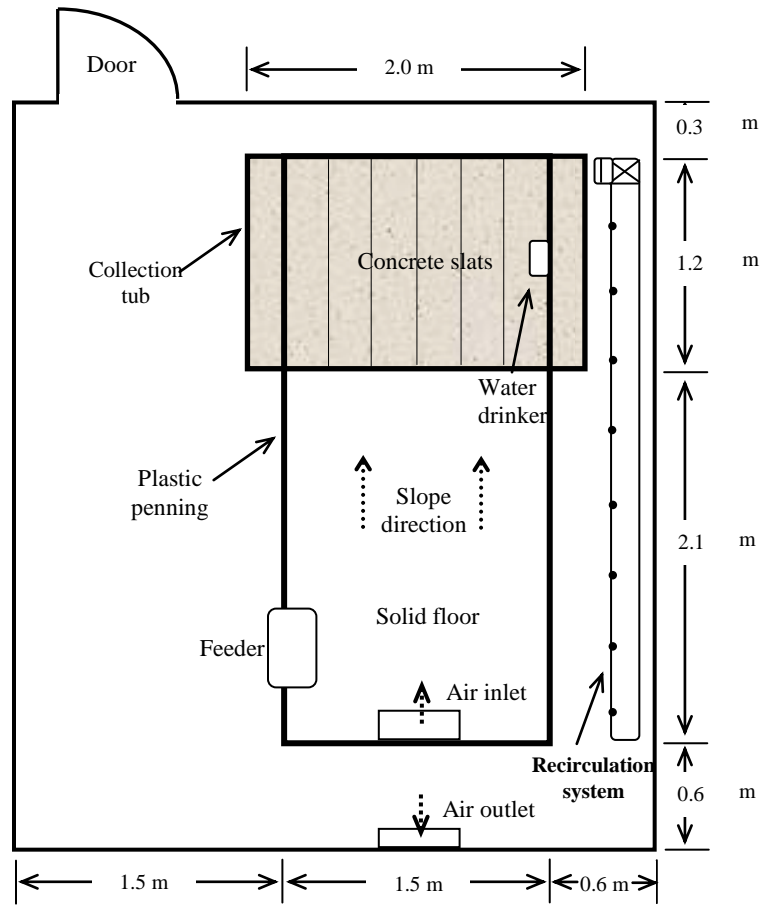
One possible application of using nanoparticles for air filtration in typical swine rooms is the installation of a filter system either in recirculation or exhaust ducts. However, considering the actual configuration of ventilation systems in existing barns, installation of the filter set-up at the exhaust would likely require significant changes to the existing ventilation system due to substantial pressure drop resulting from the filter installation. Table C.1 (Appendix C) shows the pressure drop measured across each type of filter assembly when exposed to varying face velocities. A more practical approach then would be to install the filter system as part of a recirculation system which may already be in operation in many existing barns or could be added on. With the continuous operation of the recirculation system throughout the growing period of pigs, it is possible for a treatment filter installed in a recirculation duct to continuously remove gases and contaminants in the air within the room, thereby protecting pigs and barn workers as well as minimizing the emission of pollutants to the environment. In this study, the effectiveness of the air filtration system using the most effective filter design, rated face velocity, and nanoparticle loading amount identified in the semi-pilot scale tests was investigated in the air recirculation system installed in each chamber; one with a filter pad only (Control room) and the other one with a filter loaded with zinc oxide nanoparticles (Treated room).

Test rooms and animals

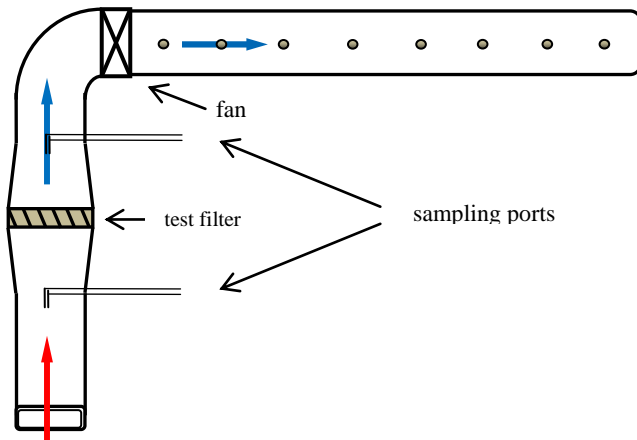
This experiment was carried out in the environmental chambers described in section 4.3.1. The management of the chambers as well as animal care and capacity were similar to that in the mixing method tests. In addition to the previously described instrumentations, a ventilation air recirculation system was installed in each chamber (Figure 4.8-A). As shown in Figure 4.8-B,

the system was operated at negative pressure relative to the chamber air space. The axial fan (Godro Multifan, Vostermans BV, IL, USA) drew in contaminated air near the manure pit and passed it through the 36-centimetre diameter galvanized sheet duct where the filter housing was installed. The filter housing was made to be square-shaped with a 38 cm x 38 cm dimension for ease in installation and to meet the required 0.5 m/s face velocity of the test filter while maintaining a 105 litres per second (Lps) output from the fan. The 0.5 m/s face velocity was identified from the semi-pilot scale tests as the most effective while the 105 Lps recirculation rate was based from the recommended recirculation rate of 7 Lps/m² of floor area for pig housing by Darby and Dill (1988). Treated air was then distributed back to the room through the 30-centimetre diameter duct connected to the downstream side of the fan. The duct had 8 equally-spaced 3.8-centimetre diameter holes which served as outlets for the treated air to flow back into the chamber airspace. Fan speed was controlled using a manual speed controller (Phason Model MSC-4, Winnipeg, Canada).

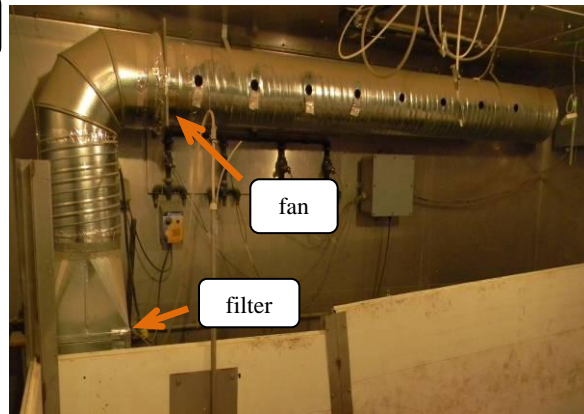
With a fluidized bed filter design and loading amount of 30 g (0.28 g/cm² of filter cross-sectional area) determined from the semi-pilot scale tests, the test filter installed in the treatment room was loaded with a total of 405 g of zinc oxide nanoparticles. The control chamber, on the other hand, had a filter pad only (not loaded with zinc oxide nanoparticles). Both filter systems had a dimension of 38 cm (L) x 38 cm (W) x 3.2 cm (T) and the same construction as the filter system used in the semi-pilot scale tests (plastic styrene with honeycomb structure). The upstream and downstream faces of the plastic structure were covered with a commercially-available filter pad material (Model HPE30621 Electrostatic Hammock filter pad, True Blue Company, LaPorte, Indiana, USA) to keep the nanoparticles within the filter.



A



B



C

Figure 4.8. Layout of the chamber with the added ventilation air recirculation system (A). Schematic diagram (B) and photo (C) of the recirculation system used in room-scale filtration experiments.

Experimental Procedure

The same procedure that was used for the mixing method was applied in these tests; duration of each trial was 30 days and the same sampling procedures were applied. Gas sampling events with manure agitation were done on the 15th, 20th, 25th and 30th day of the trial. Test filters were installed in each chamber on Day 15 right after sampling; the level of gases measured on this day served as baseline concentration for subsequent sampling events. During each sampling day, ammonia and hydrogen sulphide levels were monitored at the pit, at the animal- and human-occupied zones, and at the upstream and downstream side of the filter assembly. Air samples were collected from these locations simultaneously at 2, 5 and 10 minutes after the start of agitation. In addition, odour samples were collected at three locations in each chamber: at the pit, animal and human levels (Figure 4.7) at 2 minutes after the start of agitation.

Aside from the target gases and odour, the effect of the treatment on average daily gain (ADG) and feed intake (ADFI) of pigs were assessed. Water usage and manure production rate were also monitored. The characteristics of the manure samples taken from the collection tub of each chamber were also determined. The details of each parameter are enumerated in Table 4.1. In addition, temperature and relative humidity of air at the upstream and downstream side of the filter were monitored using temperature-humidity sensors (Hobo U12-013, Onset Computer Corp., MA, USA; accuracy of $\pm 2.5\%$). Velocity of air before the filter and after the fan (along the recirculation duct) was set to its desired setting during filter installation (Day 15) and was rechecked daily from Day 16 until the end of the trial using an air velocity meter (Model 8330 VelociCheck, TSI Incorporated, St. Paul, MN; accuracy of $\pm 5\%$) to ensure that the air velocity passing through the filter system and the flow rate delivered by the fan to the recirculation duct were within the required settings. Air flow rate was computed as the product of the average air

velocity measured and the cross-sectional area of the duct. In addition, the pressure difference across the filter system was monitored at least twice a week using a digital manometer (Model HHP-100A, Omega Engineering, Inc., Stamford, Connecticut, USA; accuracy of ± 5 Pa).

4.4 Gas and odour analysis

Gas samples in the Tedlar bags were analyzed for hydrogen sulphide and ammonia concentrations. A hydrogen sulphide monitor with electrochemical sensor (Draeger PAC III, Draeger Canada Ltd., Ontario, Canada; accuracy of $\pm 5\%$ of reading) was used for monitoring hydrogen sulphide concentration while an ammonia analyzer (Model Chillgard RT, MSA Canada, Edmonton, AB; accuracy of ± 2 ppm) was used to measure ammonia levels. As shown in Figure 4.9, these analyzers were connected in series using Teflon tubing (approximate inside diameter of 0.4 cm) so that the same gas sample was analyzed for both gases. Using a peristaltic pump (Master flex L/S tubing pump, Model 7017-52 pump head, Cole-Parmer, Vernon Hills, USA), gas samples were withdrawn from the bags and introduced to hydrogen sulphide and ammonia analyzers at a rate of 0.5 and 1.1 L/min, respectively. Flow rate requirement of the analyzers was achieved by installing flow meters (Aalborg Flowmeter, Instrument and Controls Inc., NY, USA). Prior to analysis, the gas analyzers were calibrated using standard gases and were programmed to record and store data every minute. The hydrogen sulphide monitor has an internal datalogger while the signal from the ammonia analyzer was logged in a datalogger (CR1000, Campbell Scientific, Logan Utah, USA). In addition, odour samples in 10-litre Tedlar bags were sent to commercial olfactometry laboratories (University of Manitoba, Winnipeg and University of Saskatchewan, Saskatoon for mixing and filtration tests, respectively) and were analyzed following the British standard of odour measurement (EN13725, 2003) within 30 hours after sample collection.

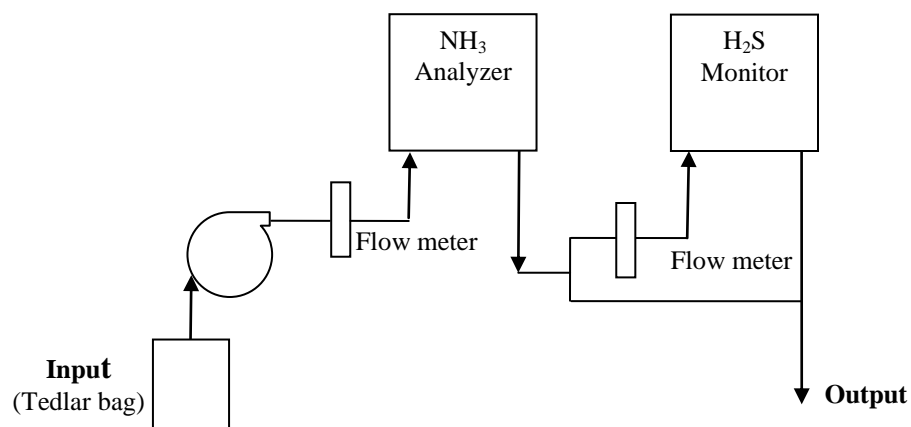


Figure 4.9. Schematic diagram of the experimental set-up used for gas analysis.

4.5 Statistical procedures

The effectiveness of mixing zinc oxide nanoparticles with the manure slurry relative to the control was analyzed using a randomized complete block (RCB) design with repeated measures. The replicate trials were considered as blocks where each block had experimental units (5 experimental totes for the semi-pilot scale tests and 2 environmental chambers for the room tests). The treatments were assigned at random once in each block. Levels of gases and odour in each experimental unit were measured over successive sampling periods.

For the filtration method with zinc oxide nanoparticles, randomized complete block design with split-plot was used to determine the most effective filter design and face velocity (Phase 1). The test filters (treatment) were considered as the main plots while filter designs and face velocity as the sub-plots. The effect of trial was the blocking factor, of which treatments were evaluated randomly. In determining the most effective loading amount (Phase 2) as well as evaluation of the

effectiveness of the treatment in room-scale tests, a randomized complete block design with repeated measures analysis was performed.

Prior to conducting the statistical analysis, the data were checked for normality using Shapiro-Wilk test. If the data followed a non-normal distribution, a log-transformation was performed before subjecting to statistical analysis. Analyses of the main and interaction effects of the independent variables (application rate, filter design and face velocity) on the dependent variable (hydrogen sulphide, ammonia and odour concentrations) were done using SAS Mixed Model procedure with $\alpha=0.05$ (SAS Institute Inc., NC, USA). If significant differences ($P<0.05$) were observed between means, a Tukey or Tukey Kramer post-hoc method was carried out to compare the means and consequently, to determine which pair of means was significantly different. Tukey test was used to minimize the probability of making at least one incorrect decision (family-wise type I error) (Mendenhall and Sincich, 2007). Mean separation was converted into letter groupings using PDMix800 Macro (Saxton, 1998).

4.6 Cost study

Cost analysis of the application of nanoparticles in a typical swine operation was undertaken after the room-scale experiments. The analysis was carried out with the assumption that the treatment was applied at the grow-finish stage of production. Thus, all the expenses incurred for one complete growth cycle in a grow-finish room including the purchase of material (nanoparticles) and equipment, as well as labour and operating costs were estimated. The total cost associated with these gas and odour control techniques was then compared to the overall cost of production.

5 RESULTS AND DISCUSSION

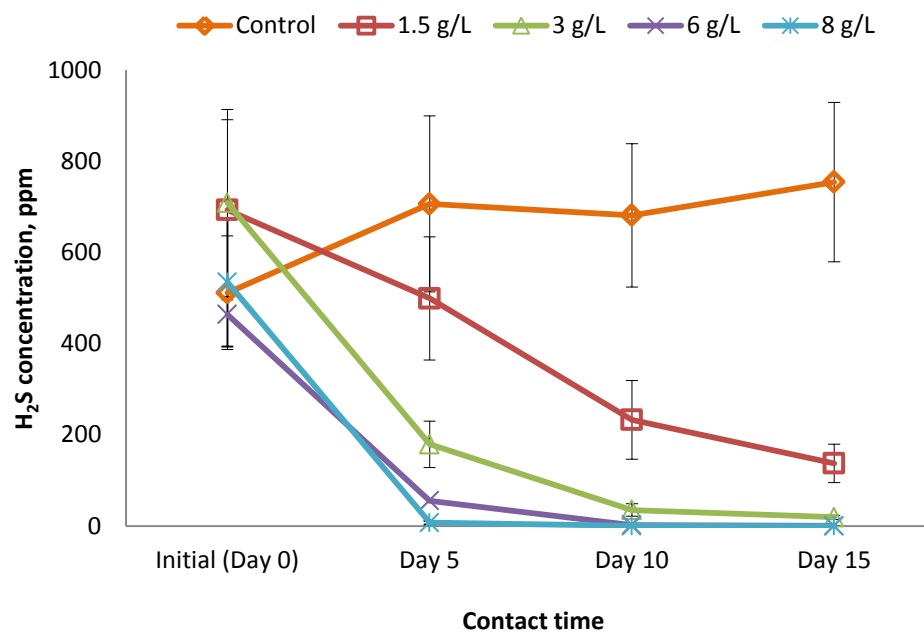
5.1 Semi-pilot Scale Tests

5.1.1 Mixing with manure slurry

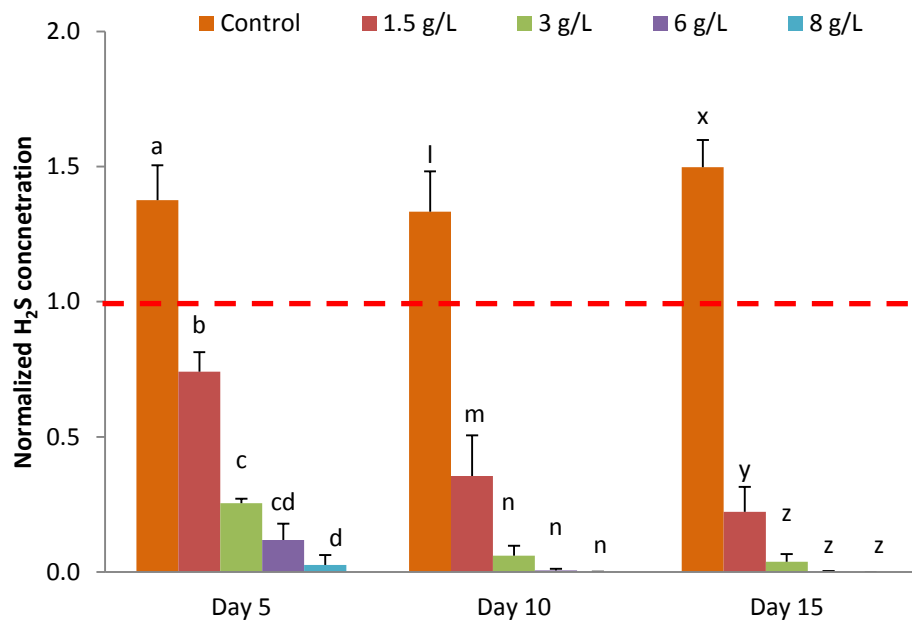
Figure 5.1-A shows the actual concentration of hydrogen sulphide emitted from the manure samples treated with zinc oxide nanoparticles and the untreated (control) samples. Levels of hydrogen sulphide in the control samples increased sharply at Day 5 and then almost leveled off until Day 15. This could be due to the decreasing amount of substrate available to bacteria as reported by Hobbs et al. (1999) when they studied the production and emission of gases and odour from ageing swine manure. Moreno (2009) had similar observations when he monitored the evolution of hydrogen sulphide production in swine manure in serum bottles wherein the concentration showed an increasing trend initially and then gradually stabilized after 1 - 2 weeks. On Day 15 after treatment application, hydrogen sulphide levels from treated systems were below 150 ppm on average while that of control reached as high as 750 ppm.

To compare results from untreated and treated manure samples, hydrogen sulphide levels were normalized as a ratio of their final and initial concentration with values much lower than 1.0 (dashed line) indicating better effectiveness in reducing the level of the target gas. Normalized concentrations, as shown in Figure 5.1-B, take into account the variations in the initial concentrations of the target gases, thus values of 0.65 and 0.30, for instance, correspond to 35 and 70% reduction relative to their initial concentration, respectively. In contrast with the

untreated manure samples, the concentration of hydrogen sulphide in the slurry treated with zinc oxide nanoparticles decreased continuously as the trial progressed. A significant reduction in hydrogen sulphide levels was observed in treated manure samples starting from Day 5 after the treatment has been applied ($P < 0.05$). On Day 15 after zinc oxide application, hydrogen sulphide concentrations of the samples treated with 3, 6 and 8 g/L of zinc oxide achieved more than 95% reduction in hydrogen sulphide levels while the 1.5 g/L treatment and the control showed 78% reduction and 50% increase, respectively. The observed decrease in hydrogen sulphide levels could be attributed to the addition of zinc oxide nanoparticles particularly since the control systems showed increasing hydrogen sulphide trends during the 15 days of monitoring. Furthermore, the results were also indicative of the persistence of the effect of the treatment because appreciable hydrogen sulphide reduction was achieved for up to 15 days after zinc oxide incorporation into the slurry.



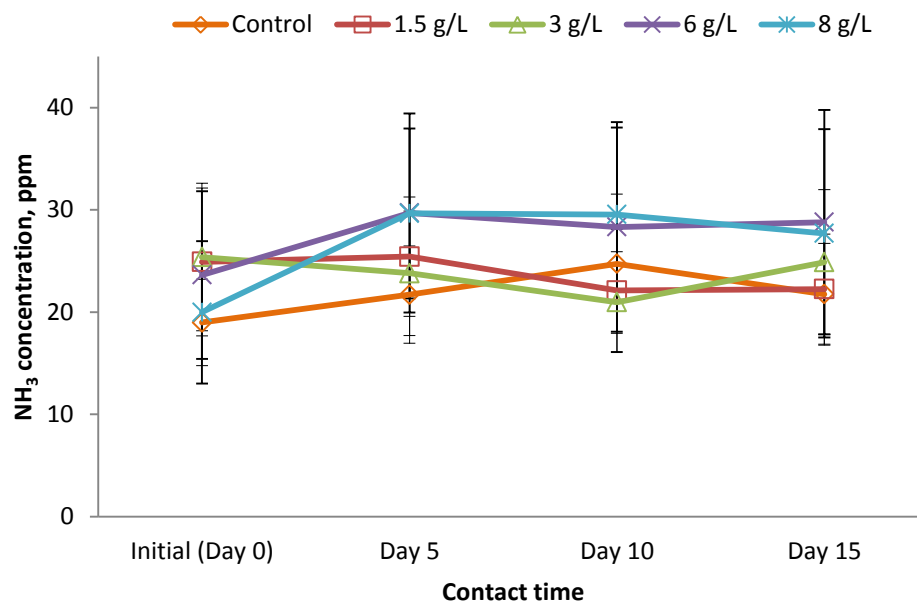
A



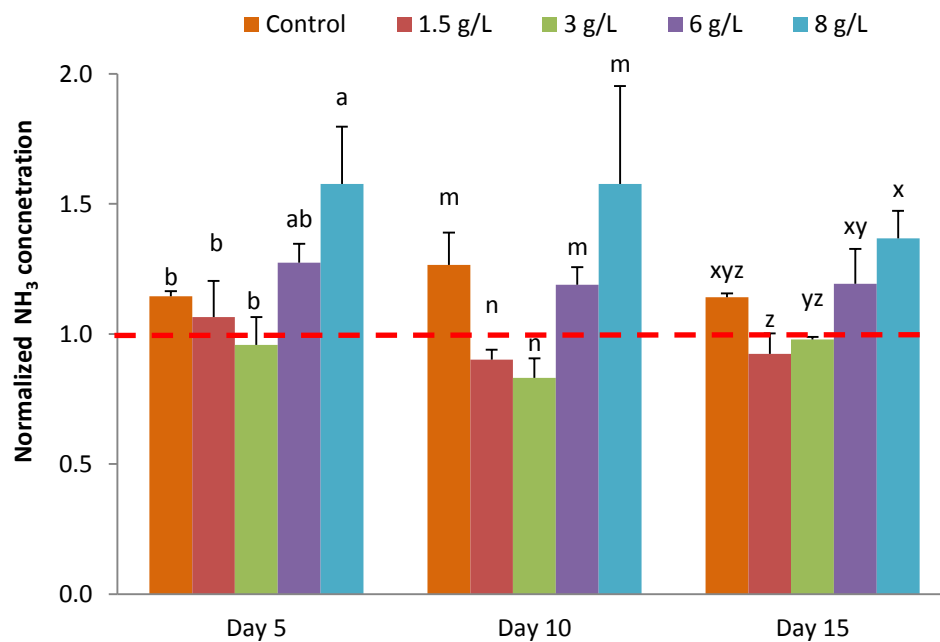
B

Figure 5.1. Mean (\pm SD) actual (A) and normalized (B) concentrations of hydrogen sulphide emitted from untreated (control) slurry and slurry mixed with zinc oxide nanoparticles at various application rates and contact time in semi-pilot scale tests, $n=3$. Means with the same letters on the same day (Figure B) are not significantly different ($P>0.05$).

On average, ammonia concentrations from all manure samples regardless of contact time ranged from 19 to 30 ppm as plotted in Figure 5.2-A. Statistical analysis showed no significant difference ($P>0.05$) in actual ammonia levels between treated and untreated manure samples. However, examination of the change in actual ammonia levels with respect to its initial value through normalization procedures as shown in Figure 5.2-B revealed significant differences among treatments including the control and was influenced by the amount of nanoparticles applied ($P<0.05$). The addition of 6 and 8 g/L of zinc oxide nanoparticles to the slurry as well as the untreated manure samples exhibited an increase in ammonia levels regardless of monitoring days, while the opposite was observed for 1.5 and 3 g/L treatments. Comparison of means among all treatments including the control showed that the manure sample with 3 g/L of zinc oxide nanoparticles applied was significantly different ($P<0.05$) from 6 and 8 g/L treatments as well as the control but not significantly different from the 1.5 g/L treatment ($P>0.05$). Over the 15-day period, the maximum ammonia reduction was only about 8% which was obtained from the samples with 3 g/L of zinc oxide nanoparticles added. This finding indicated that the addition of zinc oxide nanoparticles into the manure caused minimal effect on ammonia concentration.



A



B

Figure 5.2. Mean (\pm SD) actual (A) and normalized (B) concentrations of ammonia emitted from untreated (control) slurry and slurry mixed with zinc oxide at various application rates and contact periods in semi-pilot scale tests, $n=3$. Means with the same letters on the same day (Figure B) are not significantly different ($P>0.05$).

In order to evaluate the comparative effect of the treatment on hydrogen sulphide and ammonia and consequently, to determine the particle-to-slurry ratio that worked effectively for both gases, normalized concentrations of hydrogen sulphide and ammonia, averaged over 15 days, at various application rates were plotted against each other in Figure 5.3. It can be observed that as the nanoparticle-to-slurry ratio was increased, the effectiveness of the treatment to reduce hydrogen sulphide also increased. However, the treatment was found to be less effective in reducing ammonia. Among all treatments, 3 g/L has achieved the highest ammonia reduction. From these observations, it was apparent that the slurry treated with 3 g/L of zinc oxide nanoparticles could reduce the concentrations of both hydrogen sulphide and ammonia, thus this application rate was used in the room-scale tests of mixing method.

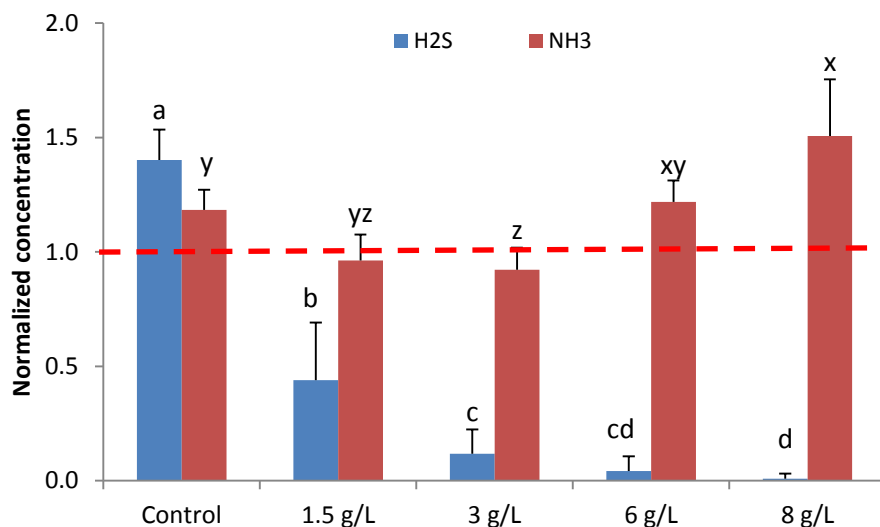
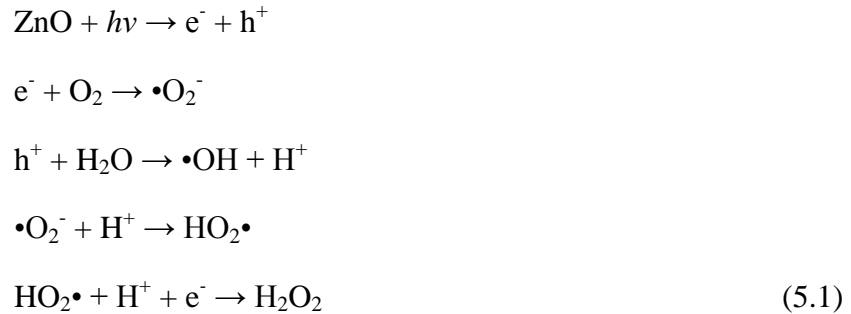


Figure 5.3. Effects of zinc oxide nanoparticles on hydrogen sulphide and ammonia expressed in normalized concentration during the semi-pilot scale tests for the mixing method, n=9. Means with the same letters on the same coloured bar are not significantly different ($P>0.05$).

Discussion of results from mixing tests

The reduction in hydrogen sulphide achieved by incorporating zinc oxide nanoparticles into the slurry could be attributed to the antibacterial activity of zinc oxide nanoparticles and the known capacity of zinc oxide for adsorption of hydrogen sulphide.

The antibacterial behaviour of zinc oxide nanoparticles involved two mechanisms: 1) distortion of the bacterial cell membrane, and; 2) production of highly reactive oxygen species (ROS). Several studies have shown that the deposition of zinc oxide nanoparticles on the surface of bacteria can cause fatal damage to bacterial cells. The damage was likely due to the surface roughness of zinc oxide nanoparticles which distorts the intracellular components of the cell and eventually disrupts cellular functions (Brayner et al. 2006; Zhang et al., 2007; Liu et al., 2009). On the other hand, the second mechanism is governed by the following reactions (Sawai et al., 2003; Fang et al., 2006; Padmavathy and Vijayaraghavan, 2008):



Under normal lighting conditions, electron-hole ($\text{e}^- + \text{h}^+$) pairs were generated by zinc oxide. Upon collisions with electron, dissolved oxygen molecules (O_2) produced superoxide radical anions ($\bullet\text{O}_2^-$). The holes split water (H_2O) molecules into hydroxyl radicals ($\bullet\text{OH}$) and hydrogen ions (H^+). The hydrogen ions generated then reacted with superoxide radicals to produce perhydroxyl radical ($\text{HO}_2\bullet$) which upon collision with electrons and reaction with other

hydrogen ions produced hydrogen peroxide (H_2O_2) molecules (Padmavathy and Vijayaraghavan, 2008). Reactive oxygen species (ROS) such as hydrogen peroxide, superoxide radical anions and hydroxyl radical, are strong oxidizing agents that can penetrate into cell membrane and eventually inhibit bacterial growth or kill bacterial cells (Fang et al., 2006; Wang et al., 2007; Zhang et al., 2007). These reactive oxygen species, as a product of incomplete oxygen reduction, are toxic to anaerobic microorganisms such as sulphate-reducing bacteria (SRB) (Brioukhanov et al., 2010) which are mainly responsible for the production of hydrogen sulphide in swine manure.

Another factor that could contribute to hydrogen sulphide reduction is the adsorption of hydrogen sulphide by zinc oxide. Zinc oxide has been used as an adsorbent of hydrogen sulphide in drilling fluids (Davidson, 2004; Sayyadnejad et al., 2008) and sewage treatment (Bagreev et al., 2001) during which the process produced water (H_2O) and an insoluble zinc sulphide (ZnS) as shown in the reaction below:



With the two modes of action exhibited by zinc oxide nanoparticles towards hydrogen sulphide as mentioned above, a complete mass balance of the chemical reaction shown in equation 5.2 would be helpful in assessing which among the antibacterial activity or adsorption capacity had the dominant effect on the reduction of hydrogen sulphide. In addition to the mass of the reactants (zinc oxide and hydrogen sulphide) which can be measured during the tests, this procedure would also require the mass of zinc sulphide and water as products of the reaction which was not realized in this present work due to some constraints such as equipment

availability. Further investigation on this area needs to be carried out in order to determine and optimize the factors responsible to the reduction in hydrogen sulphide levels.

The possible competition between hydrogen sulphide and ammonia molecules for the adsorption sites of zinc oxide could probably be the reason for the only slight reduction in ammonia concentrations achieved from manure samples mixed with zinc oxide nanoparticles. In a study conducted by Chung et al. (2005) on biological activated carbon biotrickling filter, the ammonia adsorption period was shortened due to hydrogen sulphide coexistence. Also, an increase in ammonia levels in 6 and 8 g/L treatments was observed as shown in Figure 5.3. The increase could possibly be due to excessive application of zinc oxide nanoparticles into the manure. In the desulphurization experiment of Wang et al. (2008), zinc oxide nanoparticles at higher rates blocked the active centres for adsorption causing unfavourable chemistry such as an increase in pH. In this study, an increase in pH from 7.4 to 8.8 and 8.9 was observed from manure samples with 6 and 8 g/L treatments, respectively on Day 15 after zinc oxide application (Table B.1 in Appendix B). According to Hartung and Phillips (1994), the increase in pH in swine manure led to higher conversion rates of ammonium ion to ammonia gas, thus resulting to an increase in ammonia volatilization.

5.1.2 Manure headspace gas filtration

Effect of filter design, face velocity and loading amount on hydrogen sulphide and ammonia levels

Filter design, face velocity and nanoparticle loading amount are few of the important factors that may have significant influence on the effectiveness of the filter to reduce the levels of the target gases. Filter design and nanoparticle loading amount influence the available surface

area for physical and chemical reactions while face velocity affects the length of exposure of the target gases to the nanoparticles. In this test, the effectiveness of a particular filter was assessed based on percent reduction in target gas concentrations which was computed as:

$$RE = \left[1 - \frac{C_{down}}{C_{up}} \right] \times 100 \quad (5.3)$$

where:

RE = reduction effectiveness, percent reduction in target gas concentration, %
 C_{down} = target gas concentration downstream of the filter, ppm
 C_{up} = target gas concentration upstream of the filter, ppm

Thus, percent reduction (RE) values closer to 100% signify better effectiveness in reducing gas levels. A 60% reduction for instance, would mean that a 1000 ppm gas concentration was reduced to 400 ppm after passing through the filter.

Figure 5.4 shows the percentage reduction achieved by packed bed filters at different loading amounts when exposed to manure gases at varying face velocities. Packed bed filters attained a mean hydrogen sulphide reduction of about 40 - 50% and ammonia of about 38 - 49% relative to the concentrations at the upstream side of the filter which ranged from 95 to 357 ppm of hydrogen sulphide and 18 to 42 ppm of ammonia. Mostly decreasing trends in percentage reduction were observed as face velocity increased. Lower face velocity allowed the target gases to be exposed longer to the filter media. For instance, the filter loaded with 30 g of zinc oxide nanoparticles when subjected to a face velocity of 0.2 m/s led to about 40 milliseconds (ms) of target gas exposure compared to about 10 ms of exposure at 0.8 m/s. Longer exposure to target gases would result to a higher possibility of reaction with the nanoparticles loaded into the filter. Statistical analysis, however, indicated that the differences in percent reduction in levels of target gases as face velocity increased were not significant ($P > 0.05$). In addition, no significant change

in hydrogen sulphide and ammonia reduction was observed with an increase in loading amounts ($P>0.05$). This could be attributed to particle compaction wherein the available area for surface reaction between the nanoparticles and the target gases was mainly the exposed cross-sectional area of the filter which in this case has remained constant even with an increase in loading amounts. Asis (2008) also had similar observations when she evaluated the effectiveness of the different amounts of zinc oxide nanoparticles loaded into the filter cassette assembly in reducing hydrogen sulphide and ammonia levels.

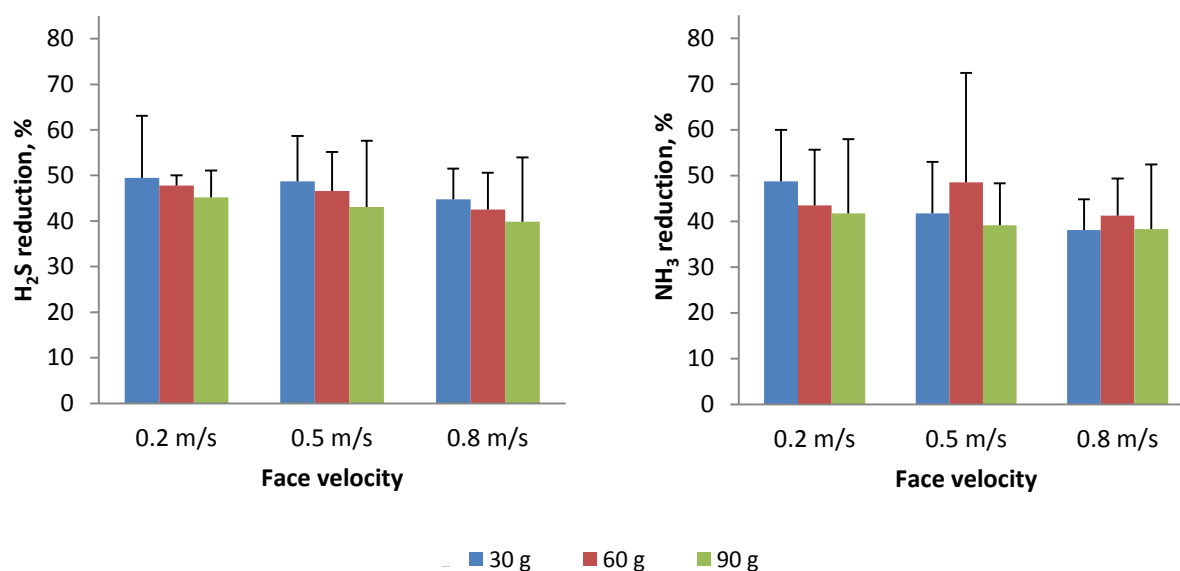


Figure 5.4. Mean (\pm SD) percent reduction in hydrogen sulphide and ammonia levels of packed bed filters loaded with zinc oxide nanoparticles at varying face velocities during the semi-pilot scale tests for the filtration method, $n=3$. Effects of face velocity and loading amount on H_2S and NH_3 reduction were not statistically significant ($P>0.05$).

On average, fluidized bed filters achieved a 49 - 79% decrease in hydrogen sulphide and a 39 - 57% decrease in ammonia relative to their upstream concentrations of 95 - 330 ppm hydrogen sulphide and 20 - 42 ppm ammonia (Figure 5.5). For hydrogen sulphide, face velocity had significant impact on percent reduction ($P<0.05$). Highest percent reduction was attained

when the gas stream was passed through the filters at a face velocity of 0.5 m/s. This reduction was not statistically different from 0.2 m/s ($P>0.05$) but significantly different from 0.8 m/s ($P<0.05$). The face velocity of 0.5 m/s or less possibly allowed a more fluidized-bed behaviour of zinc oxide nanoparticles when the manure gas stream passed through the filter, resulting to better surface reaction between the particles and the target gases. It was also observed that for these velocities (0.5 m/s and 0.2 m/s), a filter loaded with 30 g of zinc oxide nanoparticles achieved the highest reduction in both gases.

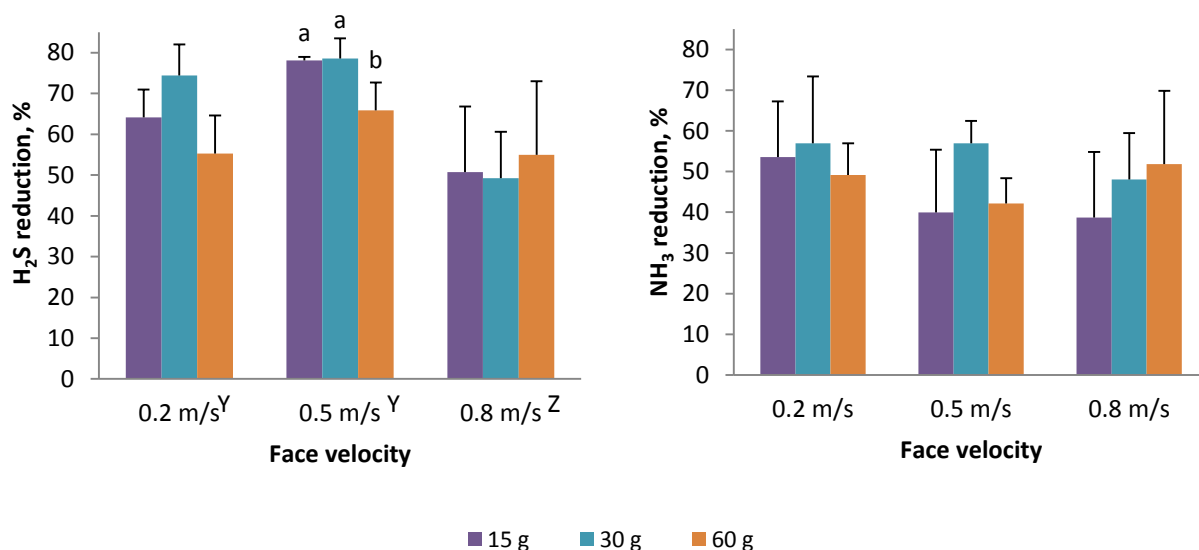


Figure 5.5. Mean (\pm SD) percent reduction in hydrogen sulphide and ammonia levels of fluidized bed filters loaded with zinc oxide nanoparticles at varying face velocities during the semi-pilot scale tests for the filtration method, $n=3$. Means with the same letters within the same face velocity are not significantly different ($P>0.05$). Face velocity levels with the same letters are not significantly different ($P>0.05$).

As described in section 4.2.2, a commercially-available filter pad material (Model HPE30621 Electrostatic Hammock filter pad, True Blue Company, LaPorte, Indiana, USA) was used to hold the nanoparticles within the filter for both packed and fluidized bed filter designs

evaluated in these tests. In order to account for the reduction caused by this filter pad material, a filter pad only (not loaded with zinc oxide nanoparticles) was included in the assessment of filters and was also subjected to similar face velocities. Figure 5.6 shows the performance of the filter pad in reducing the levels of the target gases. On average, the filter pad reduced hydrogen sulphide and ammonia levels up to 18 and 21%, respectively. Gas molecules were likely trapped into the pores of the filter pad material through electrostatic attraction, thus causing the reduction. It was also observed that the gas reduction achieved by the filter pad material decreased as the face velocity increased. Similar to the trends observed for other filter systems, slower face velocity translates to a longer contact time between the filter pad and the target gas molecules.

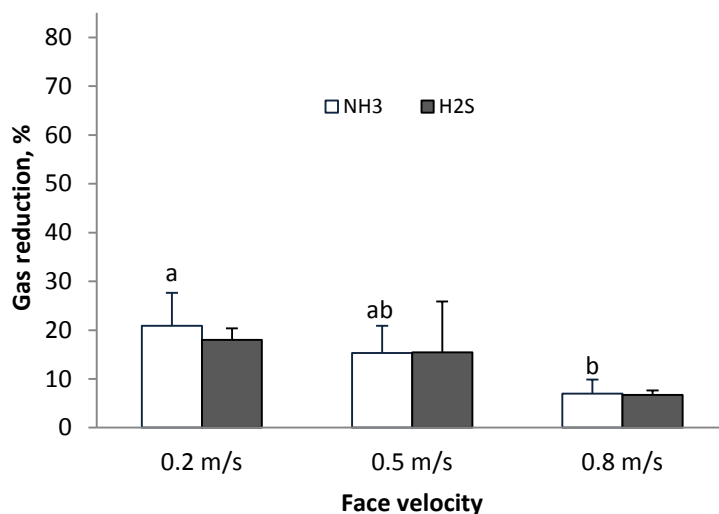
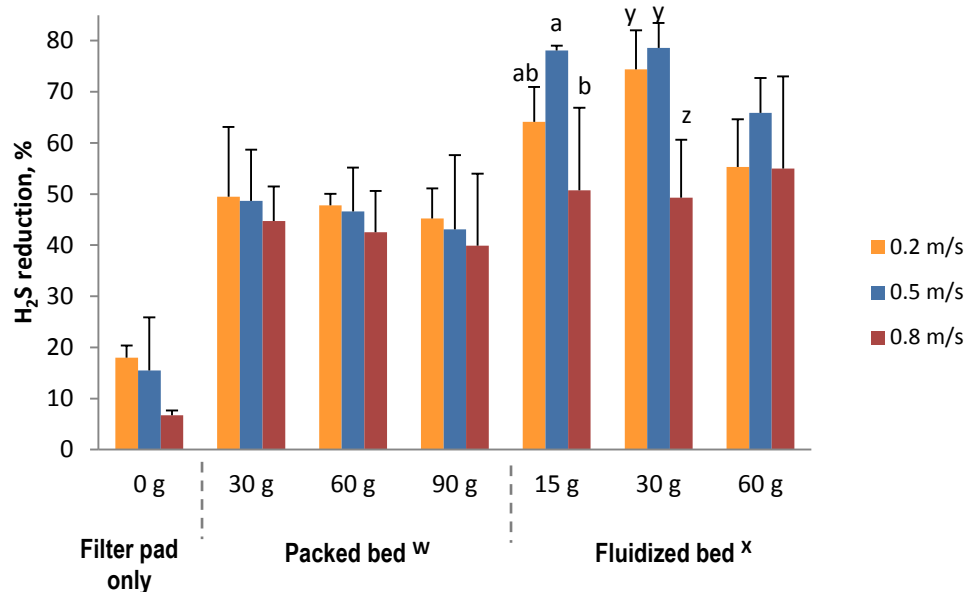
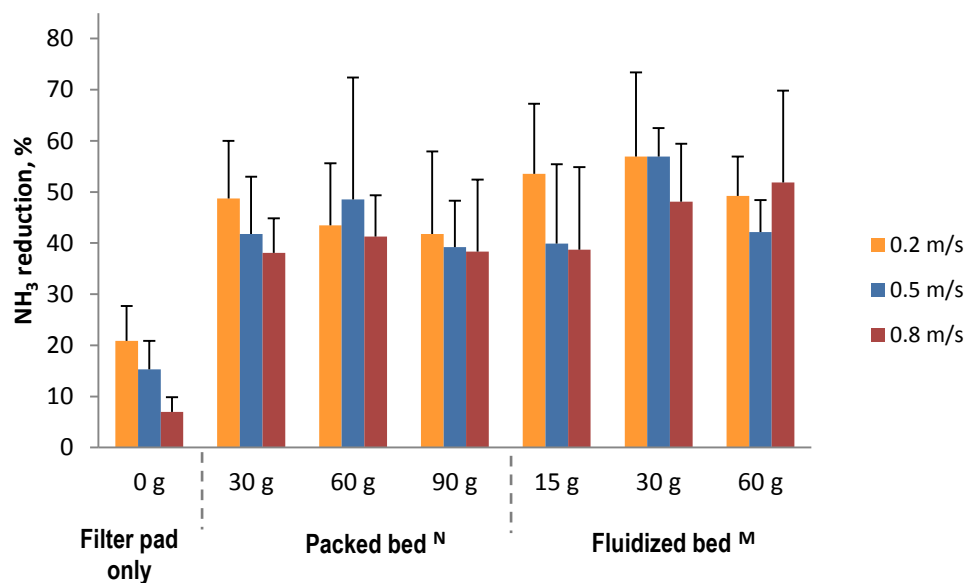


Figure 5.6. Mean (\pm SD) percent reduction in hydrogen sulphide and ammonia levels of filter pad only (not loaded with zinc oxide nanoparticles) at varying face velocities during the semi-pilot scale tests for filtration method, $n=3$. Means with the same letters on the same coloured bar are not significantly different ($P>0.05$).

A consolidated plot of the performance of the various test filters is shown in Figure 5.7. All filters loaded with zinc oxide nanoparticles were able to reduce hydrogen sulphide by about 40 - 79% and ammonia by 38 - 57%. These reductions were significantly higher than those by filter pad only ($P < 0.05$) which showed 7 - 18% decrease in hydrogen sulphide and 7 - 21% decrease in ammonia. Thus, excluding the effect of the filter pad material, zinc oxide nanoparticles achieved a maximum of 61% reduction in hydrogen sulphide and 36% in ammonia. Among treated filters, fluidized bed filters were significantly more effective in reducing the levels of both gases than packed beds regardless of loading amount ($P < 0.05$). This can be attributed to the extra air spaces in fluidized bed designs that allowed the nanoparticles to be in fluid-like state when manure gases passed through the filter. The fluid-like behaviour of the nanoparticle-gas mixture provided more exposed surface area for physical and chemical reactions, thus resulting in a greater reduction in target gas levels. Unlike ammonia, hydrogen sulphide reduction was significantly affected by filter face velocity. Highest decrease in hydrogen sulphide levels were observed from filter samples exposed to 0.5 m/s. Statistical analysis revealed that this reduction was significantly different from 0.8 m/s ($P < 0.05$) but not with 0.2 m/s ($P > 0.05$). Thus, among all the operational factors tested, a fluidized bed filter exposed to a face velocity of 0.5 m/s led to the highest significant reduction in hydrogen sulphide and ammonia levels.



A



B

Figure 5.7. Combined plots of mean (\pm SD) percentage reduction in hydrogen sulphide (A) and ammonia (B) levels of two types of filters loaded with zinc oxide nanoparticles and filter pad only at varying face velocities during the semi-pilot scale tests for the filtration method, $n=3$. Means with the same letters on the same loading amount within the same filter design are not significantly different ($P>0.05$). Comparisons between packed bed and fluidized bed filter designs were limited to 30 and 60 g loading amounts. Filter designs with the same letters are not significantly different ($P>0.05$).

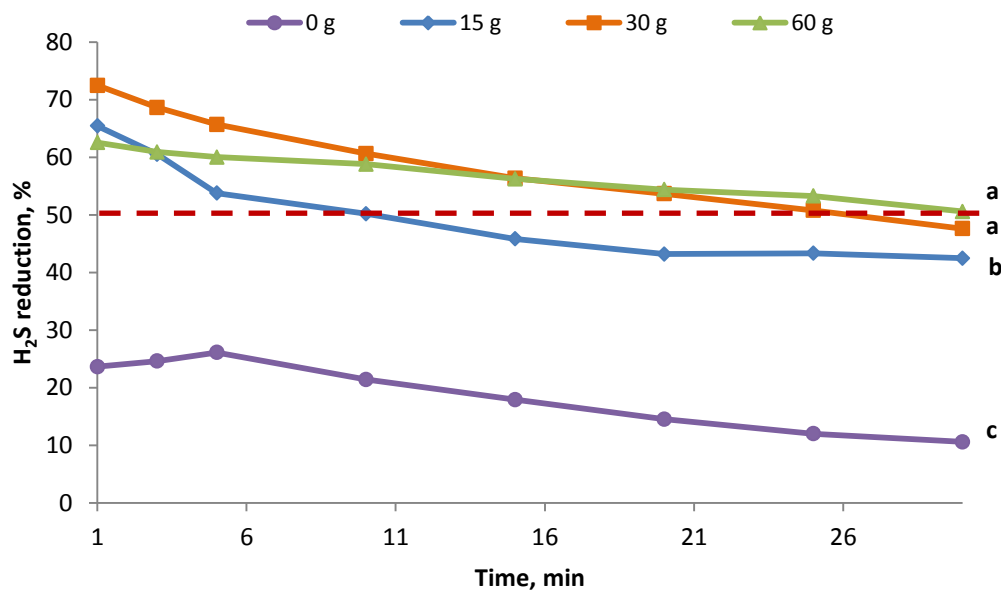
The percentage reduction in hydrogen sulphide and ammonia achieved by the test filters (Figure 5.7) may have been affected by the upstream (inlet) concentrations of the target gases. While this effect would have been desirable to investigate, this would have required tests with levels of inlet concentrations of the target gases set at specified levels, which was a challenge to achieve due to the variable nature of the manure gases as evident in the actual levels of target gases measured at the upstream side of the filter shown in Figures C.1 and C.2 (Appendix C). With the available data on hand, it was observed that face velocity had a significant effect ($P < 0.05$) on the inlet concentrations of hydrogen sulphide and ammonia introduced into the filter. The 0.2 m/s face velocity which was equivalent to 100 L/min flow rate had higher inlet gas concentrations compared with 0.8 m/s (400 L/min). This could be due to dilution of the manure gases from the headspace of the manure buckets used as sources with fresh make-up air required to attain the specified face velocity. It is important to note, however, that the inlet concentrations of the target gases were measured immediately upstream of the filter, not at the gas source (manure bucket) where the dilution took place.

Evaluation of breakthrough performance of selected test filter system

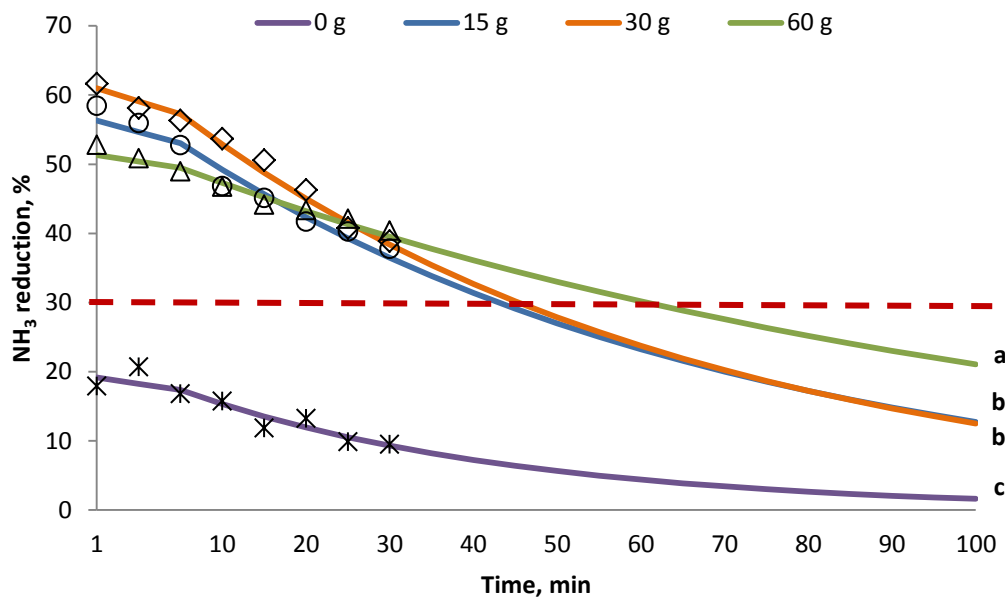
Having identified the fluidized bed filter design and 0.5 m/s filter face velocity as the most effective test parameters, phase 2 tests were carried out to further evaluate the performance of the filter in reducing the levels of the target gases over an extended period of time. The effect of the filter on hydrogen sulphide was assessed based on 50% breakthrough time while that on ammonia was based on 70% breakthrough time. Breakthrough times have been used in various studies for assessing filter performance in reducing gaseous contaminants (Guo et al., 2006; Lee et al., 2006). Fifty (50) and seventy percent (70%) breakthrough times referred to the duration of time it took for the filter's initial performance to decrease down to 50 and 30% reduction,

respectively, relative to the initial (upstream) concentration. Hydrogen sulphide was set at a higher level than ammonia because of its lower exposure limits. Thus, the longer the breakthrough time for a filter, then the filter would be considered to be more effective.

Figure 5.8 presents the performance of each filter as a function of time. For a 30-minute exposure at 0.5 m/s velocity corresponding to a flow rate of 250 L/min, all treated filters showed decreasing trends in percent reduction as exposure time progressed. These reductions in hydrogen sulphide and ammonia levels were significantly different from filter pad only ($P < 0.05$). As shown in Figure 5.8-A, on the first minute of gas exposure, 30 g of zinc oxide nanoparticles reduced hydrogen sulphide by about 72%, which gradually decreased to 50% after 26 minutes. The filter with 15 g of nanoparticles, on the other hand, achieved about 65% hydrogen sulphide reduction initially and showed a sharp decrease afterwards resulting to a shorter breakthrough time of 10 min. The sharp decrease could be attributed to the lesser amount of nanoparticles in the filter which more likely became fully saturated with the target gas molecules faster. The 60 g filter had the lowest initial hydrogen sulphide reduction but had the longest breakthrough time (about 30 min) among all filters. The decrease in percent reduction with time was very gradual which could be attributed to the greater number of sites available for surface reaction due to the larger amount of nanoparticles in the filter.



A



B

Figure 5.8. Breakthrough curves for hydrogen sulphide (A) and ammonia (B) in manure gases passed through filters with varying loading rates of zinc oxide nanoparticles, $n=3$. Curves with the same letters are not significantly different ($P>0.05$).

Over the 30-minute exposure to manure gases, the 70% ammonia breakthrough time was not reached for all treated filters. In order to evaluate the filter impact on ammonia at 70% breakthrough time, an exponential line was fitted to the actual data points as shown in Figure 5.8-B. Regression lines for all treated filters had a coefficient of determination (R^2) of more than 96%. Based on the fitted line, the estimated 70% breakthrough time was about 61 min for 60 g of zinc oxide, 45 min for 30 g of zinc oxide, and 43 min for 15 g of zinc oxide. Similar to hydrogen sulphide, the 60 g filter had the longest 70% breakthrough time even though its initial reduction was already close to 50%, the lowest among all treated filters. In addition, the filter loaded with 30 g of zinc oxide nanoparticles achieved the highest reduction in both hydrogen sulphide and ammonia among all filters on the first minute of gas exposure. This finding was consistent with the results from phase 1 tests which indicated that the 30 g - 0.5 m/s combination attained more fluid-like behaviour of the nanoparticle-air mixture. As shown in Figure 4.4-C, filters with 15, 30 and 60 g of zinc oxide nanoparticles had about 13, 25 and 50% of the 3.2 cm total depth of the filter housing filled with the nanoparticles, respectively. Compared to the filters with lower loading rate, the available free air space for the 60 g filter might have been too small for the particles to be in full fluidized suspension resulting to lesser surface contact with the target gases. The untreated filter, however, did not even reach 30% reduction for both gases at the first minute of exposure. Similar to phase 1, the difference in gas reduction between untreated and treated filters can be attributed to the zinc oxide nanoparticles loaded into the treated filters.

Based on 50% hydrogen sulphide and 70% ammonia breakthrough times, the filter with 60 g of zinc oxide nanoparticles exhibited better performance compared with 30 and 15 g filters. However, it was observed that the increase in 50% hydrogen sulphide and 70% ammonia breakthrough times from 30 to 60 g of zinc oxide nanoparticles was only about 15 and 36%,

respectively. This indicated that doubling the amount of nanoparticles loaded into the filters (from 30 to 60 g) did not lead to a proportional doubling in the filters' performance. Thus, considering the economics of treatment application in addition to its effectiveness in reducing gas levels, the 30 g filter (0.28 g/cm^2) was considered to be the most effective among all test filters.

Discussion of results from filtration tests

Physical adsorption and chemisorption are the two main processes involved in removing gaseous pollutants in the airstream (EPA, 2009). Physical adsorption is the deposition of target gas molecules (adsorbate) on the surface of the adsorbents. The interactions between the gas molecules and the adsorbents are dependent on the porosity of the adsorbent, not on the chemical nature of either the gas or the adsorbents (Bandosz and Petit, 2009). Chemisorption, on the other hand, is a chemical adsorption process where the surface of the adsorbent chemically reacts with the target gas (Bandosz and Petit, 2009; EPA, 2009).

In the filtration experiments, zinc oxide nanoparticles were able to significantly reduce the concentrations of hydrogen sulphide and ammonia. The reduction in hydrogen sulphide levels achieved after passing through the filter with zinc oxide could probably be due to chemisorption process that occurred between hydrogen sulphide and zinc oxide as described in equation 5.2. This reaction showed that hydrogen sulphide can react with zinc oxide to form insoluble zinc sulphide and water. Sanchez et al. (2005) and Wang et al. (2008) have proven this reaction mechanism when they investigated the removal of hydrogen sulphide from gaseous stream using zinc oxide nanoparticles and other zinc-based sorbents.

Unlike hydrogen sulphide, limited information on the reaction kinetics between zinc oxide and ammonia can be found in literature. Due to the smaller molecular size of ammonia (3Å), it is possible that the molecules were easily adsorbed onto the surface of zinc oxide, thus causing the reduction. This physical adsorption process could also explain the lower ammonia reduction achieved by zinc oxide filters compared with hydrogen sulphide reduction. According to Masel (1996) as cited by Bandosz and Petit (2009), physical adsorption is a weaker interaction compared with chemisorption.

Investigation of the surface chemistry of zinc oxide nanoparticles which was beyond the scope of this study should be done in order to determine the reaction mechanism of zinc oxide nanoparticles on hydrogen sulphide and ammonia, thus possibly helping in enhancing its effectiveness in reducing the levels of these target gases.

5.2 Room-scale Tests of Mixing and Filtration Treatments

The results and observations from the room-scale tests for both mixing and filtration methods using zinc oxide nanoparticles are presented side by side in the following sections. It is important to note that during the room-scale experiments, the two deployment techniques followed similar experimental procedures although they were conducted at different timeframes. In the evaluation of each deployment method, one chamber was configured as a Control to represent the commercial swine production setting.

5.2.1 Effect on hydrogen sulphide concentrations

Figure 5.9 shows the actual concentrations of hydrogen sulphide from the samples collected at 2 minutes from the start of agitation in the control and treated chambers for both mixing and filtration experiments. The concentrations of hydrogen sulphide at 2 minutes after the start of agitation are presented because these represent critical levels which could cause exposure concerns compared with the gas levels measured at 5 and 10 minutes after the start of agitation. To account for the non-homogenous nature of manure (Ndegwa and Zhu, 2003) and the inherent variation in the initial concentration of manure gases, gas samples were collected at the different locations in each chamber prior to the application of zinc oxide nanoparticles (in the treated chamber). The hydrogen sulphide concentrations on this day were plotted as Day 0 values which served as baseline for subsequent sampling events.

In the treated chamber of the mixing tests, initial hydrogen sulphide concentrations of 596, 57 and 39 ppm at the pit, animal and human levels, respectively, were reduced significantly ($P < 0.05$) to 5, 1 and 1 ppm, respectively, on Day 5 after zinc oxide nanoparticles were applied into the manure (Figure 5.9). These levels were almost unchanged to Day 15 which implied that the effect of the treatment in reducing hydrogen sulphide levels was persistent up to 15 days. On the other hand, the concentrations of hydrogen sulphide at the different sampling locations (pit, animal and human levels) in the untreated (control) chamber were not significantly different ($P > 0.05$) from each other over the 15-day monitoring period. On average, hydrogen sulphide concentrations ranged from 617 to 877 ppm, 39 to 75 ppm, and 32 to 62 ppm at the pit, animal and human levels, respectively.

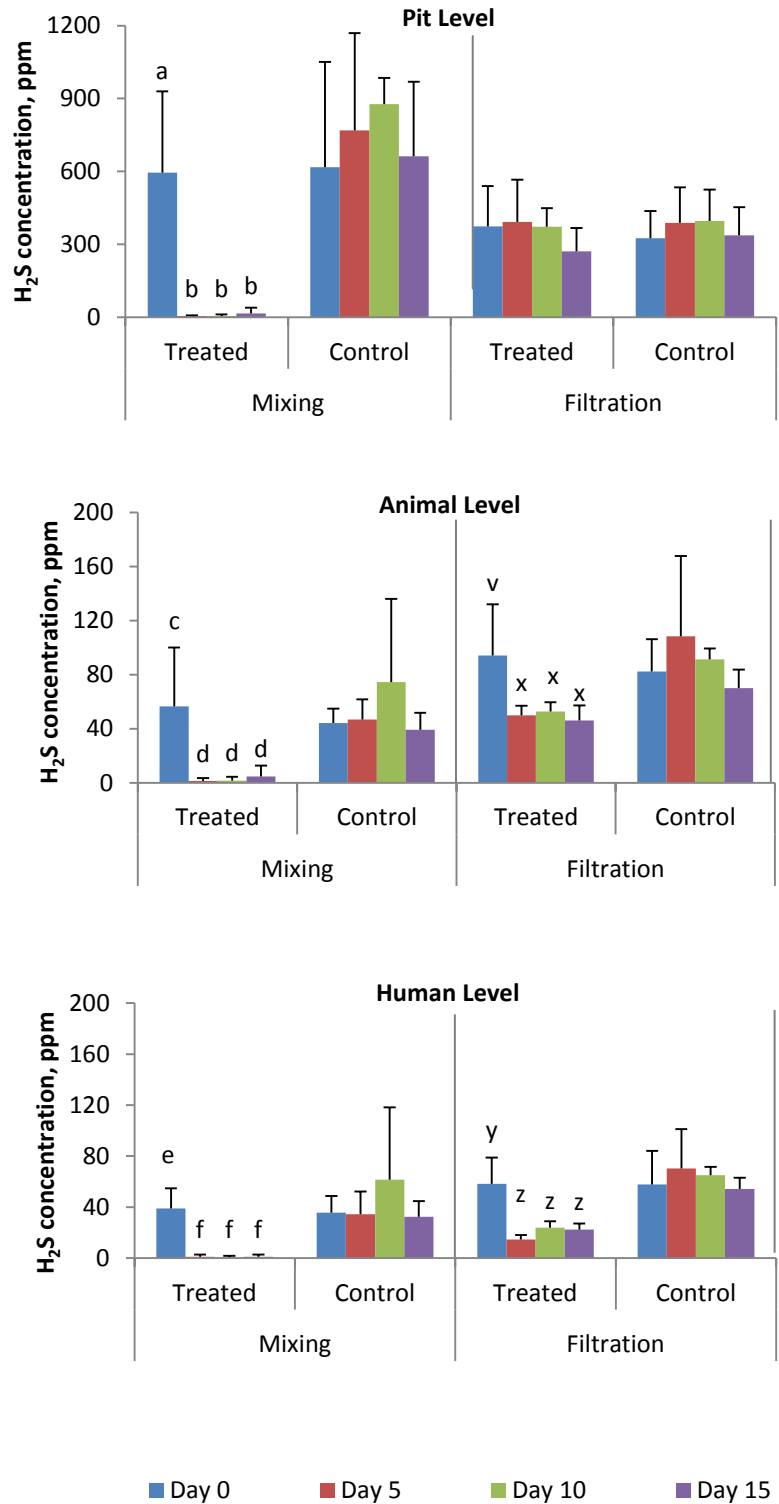
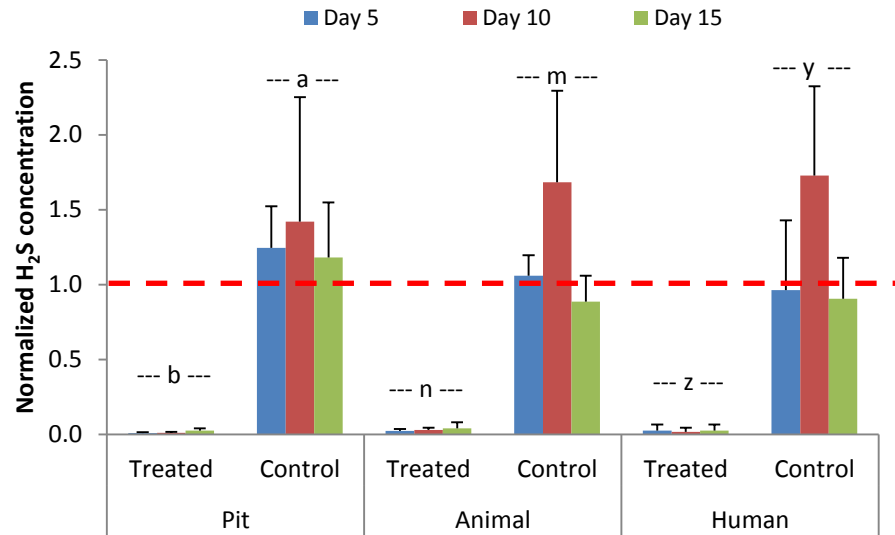


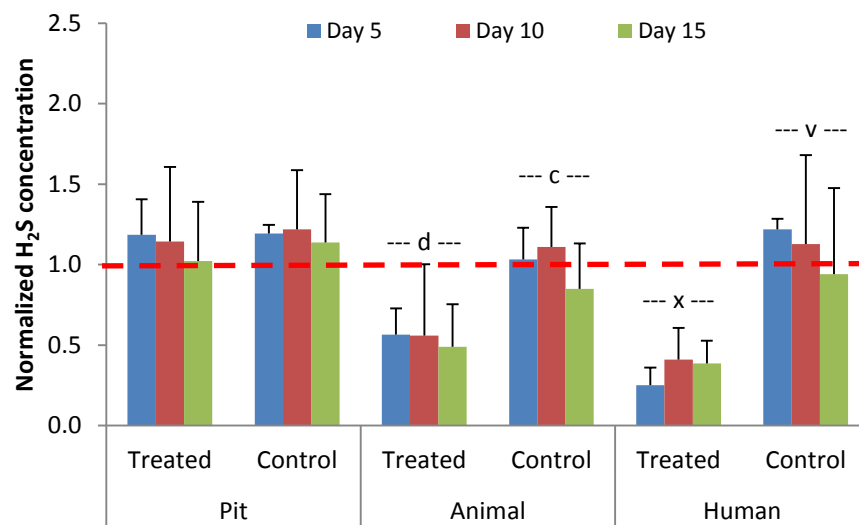
Figure 5.9. Mean (\pm SD) concentrations of hydrogen sulphide in gas samples collected from the pit, animal and human levels in the untreated (control) and treated chambers during the room-scale tests for mixing and filtration methods, $n=3$. Means with the same letters within the same sampling location in each chamber are not significantly different ($P>0.05$).

In the filtration tests, the concentrations of hydrogen sulphide over the manure pit in the chamber with zinc oxide filter (Treated) followed similar trend as that in the chamber with filter pad only (Control) as shown in Figure 5.9. This was expected considering that the air filtration system installed in the chambers was intended to treat the target gases after they have been released from the source (pit). At the animal and human zones, however, significant reduction ($P<0.05$) in the concentrations of hydrogen sulphide relative to their initial concentrations was observed in the treated chamber unlike in the control chamber which showed no significant change ($P>0.05$) even with the installation of the ventilation air recirculation system with filter pad only. Initially, mean hydrogen sulphide concentrations at the animal- and human-occupied zones in the treated chamber were 94 and 58 ppm, respectively, and decreased to 46 and 23 ppm on Day 15 after the filter with zinc oxide nanoparticles has been installed.

In order to further assess the impact of mixing and filtration treatments with zinc oxide nanoparticles, concentrations of hydrogen sulphide in each chamber on Days 5, 10, and 15 were normalized by dividing each with their corresponding initial values measured on Day 0 and plotted in Figure 5.10. Normalized values much lower than 1.0 (dashed line) indicate greater reduction in hydrogen sulphide concentrations relative to the Day 0 values. As shown in Figure 5.10-A, the addition of zinc oxide nanoparticles at a rate of 3 g/L showed significant reduction in hydrogen sulphide levels by more than 95% at the pit level as well as at the animal- and human-occupied zones ($P<0.05$), while the levels in the control chamber remained high (relative to Day 0 values) for the various sampling locations.



A



B

Figure 5.10. Mean (\pm SD) normalized concentrations of hydrogen sulphide in gas samples collected from the different sampling locations in the untreated (control) and treated chambers during the room-scale tests for mixing (A) and filtration (B) methods, $n=3$. Means with the same letters within the same sampling location are not significantly different ($P>0.05$).

The operation of the ventilation air recirculation system with zinc oxide filter in the treated chamber resulted to about 46 and 65% reduction in hydrogen sulphide concentrations at the animal and human levels, respectively (Figure 5.10-B). These reductions can be attributed mainly to the installation of the filter with zinc oxide nanoparticles in the treated chamber since the control exhibited opposite trends. It is important to note that both chambers had similar configurations and operations of the recirculation system; they just differed in the type of filter installed, i.e., filter pad only in the control vs. fluidized-bed filter with nanoparticles in the treatment chamber.

5.2.2 Effect on ammonia concentrations

Actual levels of ammonia at the pit, animal and human-occupied zones in each chamber during mixing and filtration experiments are plotted in Figure 5.11. Each data bar in the figure represents the gas concentrations from samples collected at 2 minutes after the start of agitation. In the treated chamber of the mixing tests, a slight decrease in the concentrations of ammonia at the different sampling locations (pit, animal and human levels) was observed after the addition of zinc oxide nanoparticles into the manure slurry. On Day 0, mean ammonia concentrations at the pit, animal and human zones in the treated chamber were 25, 15 and 13 ppm, respectively, and decreased to 19, 11 and 10 ppm on Day 10 after treatment application. Ammonia concentrations observed in each sampling level after the nanoparticles has been applied were not significantly different ($P>0.05$) from their initial (Day 0) values. The levels of ammonia in the control chamber were also unchanged during the 15 days of gas monitoring. On average, ammonia concentrations at the pit, animal and human levels ranged from 19 to 33 ppm, 10 to 11 ppm, and 10 to 11 ppm, respectively.

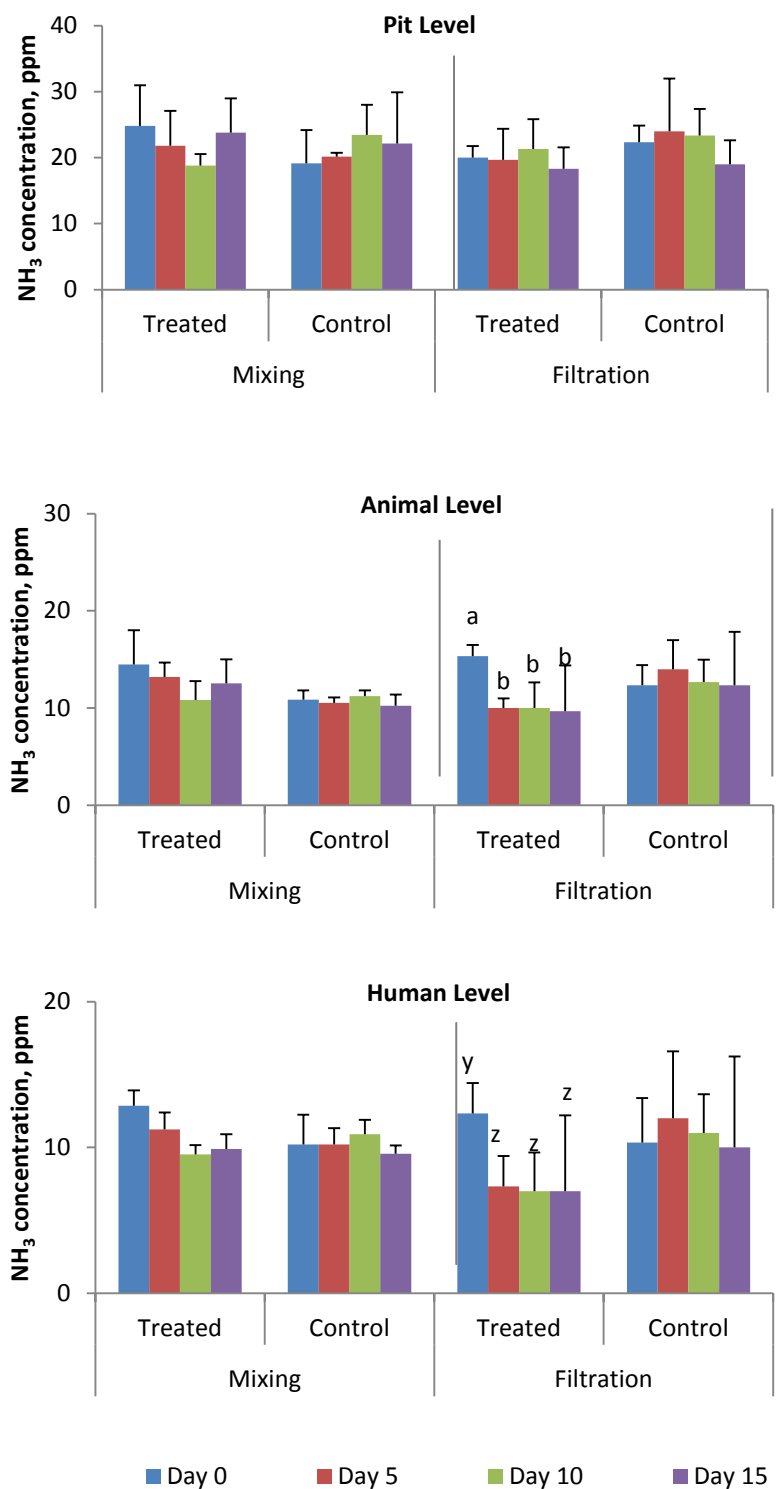
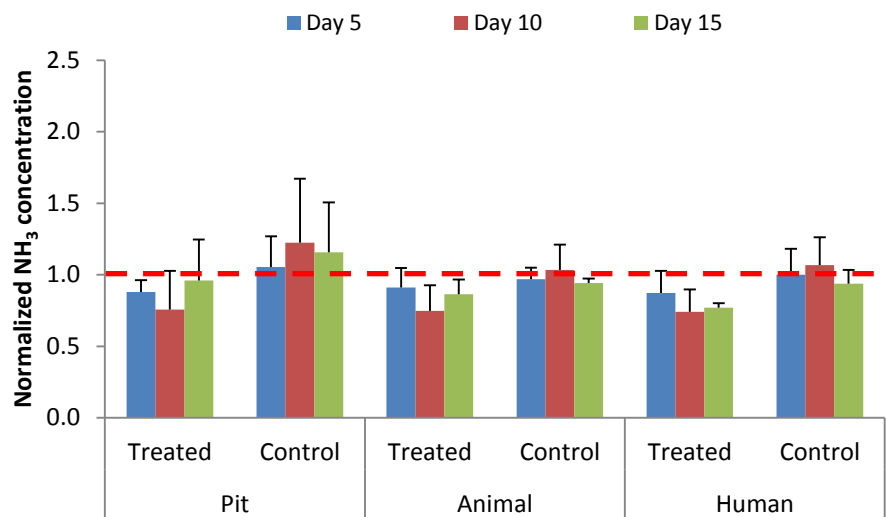


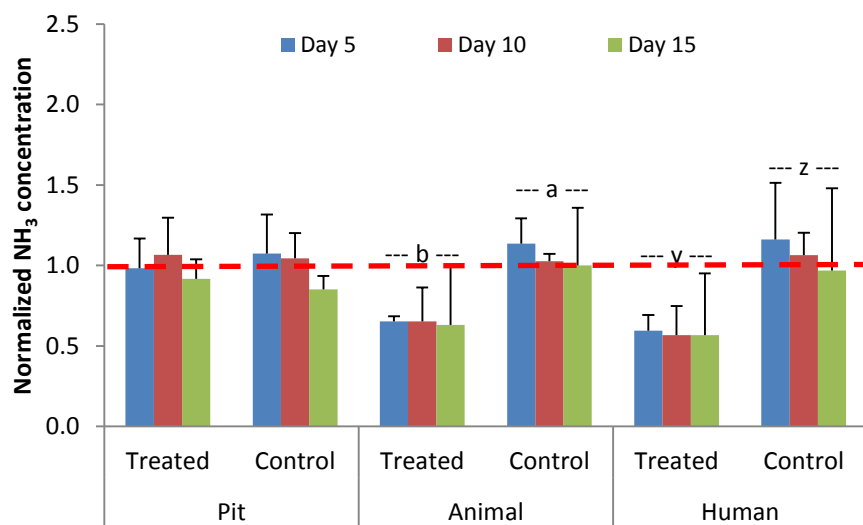
Figure 5.11. Mean (\pm SD) concentration of ammonia in gas samples collected from the pit, animal and human levels in the untreated (control) and treated chambers during the room-scale tests for mixing and filtration methods, $n=3$. Means with the same letters within the same sampling location in each chamber are not significantly different ($P>0.05$).

Prior to the operation of the air recirculation system with filter pad only in the control chamber (Day 0), ammonia concentrations at the pit, animal and human levels were 22, 12, and 10 ppm, respectively. On subsequent sampling days after filter installation (Day 5 to Day 15), no significant change was observed in ammonia concentrations at each sampling location ($P>0.05$) in the control chamber (Figure 5.11). Similar to the control chamber, ammonia concentrations at the pit level in the treated chamber were not significantly different over time ($P>0.05$). However, the addition of an air filtration system with zinc oxide nanoparticles in the treated chamber led to a significant reduction ($P<0.05$) in the concentrations of ammonia at the animal and human zones relative to their respective initial values. At the animal and human levels, initial mean ammonia concentrations were 15 and 12 ppm, respectively, which decreased to 10 and 7 ppm, respectively, on Day 15 after the installation of the filter with zinc oxide nanoparticles.

The application of zinc oxide nanoparticles into the manure slurry in the treated chamber during the mixing tests did not result to a significant reduction ($P>0.05$) in ammonia levels at the pit, animal- and human-occupied zones as evident in the normalized values of the target gas presented in Figure 5.12-A. The normalization procedure, which takes into consideration the differences in the initial gas levels, was achieved by taking the ratio of the final (Days 5, 10 or 15) and initial concentrations (Day 0). As shown in Figure 5.12-B, a reduction of about 36 and 42% in ammonia concentrations at the animal and human levels, respectively, in the treated chamber was achieved during the filtration experiments. Similar to hydrogen sulphide, these reductions can be due to the continuous operation of the ventilation air recirculation system with zinc oxide filter since the control showed mostly increasing trends throughout the 15-day monitoring period.



A



B

Figure 5.12. Mean (\pm SD) normalized values of ammonia in gas samples collected from the different sampling locations in the untreated (control) and treated chambers during the room-scale tests for mixing (A) and filtration (B) methods, $n=3$. Means with the same letters within the same sampling location are not significantly different ($P>0.05$).

As shown in Figures 5.9 and 5.11, hydrogen sulphide and ammonia levels at the different sampling locations in the control chambers for both mixing and filtration tests were almost constant from Day 0 to 15. These observations indicated that the 5-day interval between sampling events was sufficient to allow re-stabilization of the manure properties and regeneration of the target gases (after being disturbed during agitation) for the next sampling session. Also, these results implied that the installation of a ventilation air recirculation system with filter pad only had no significant impact on hydrogen sulphide and ammonia levels at the animal- and human-occupied zones during the filtration experiments.

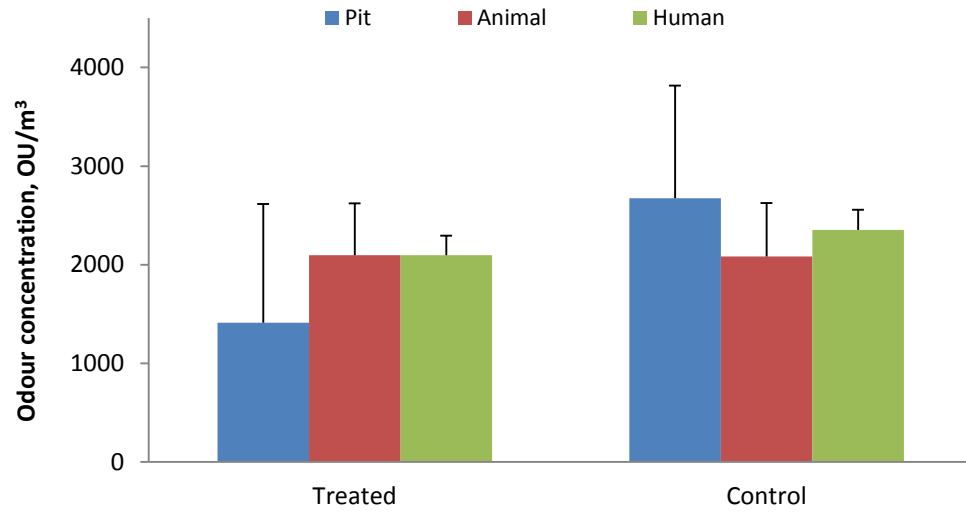
Table 5.1 shows the variations of the concentrations of the target gases with increase in sampling elevation. In both mixing and filtration tests, levels of hydrogen sulphide and ammonia at the pit were significantly higher ($P < 0.05$) than those observed at the animal and human zones. This observation, which was more evident in the control chamber, was likely due to the minimal air exchange in the underfloor pit area and the dilution of the emitted gases with ventilation air at the animal and human zones. In addition, it was observed that the reduction of hydrogen sulphide and ammonia at the human-occupied zone in the treated chamber during the filtration experiments were higher than those at the animal level. This could be due to the air movement in the chamber during sampling. As shown in Table C.2 (Appendix C), about 44% of hydrogen sulphide and 68% of ammonia emitted from the manure at the pit were drawn in by the fan; the remainder may go upward through the floor slats and most likely be captured at the animal level which was about 0.5 m above the pen floor. On the other hand, the recirculation duct expelled treated air that passed through the zinc oxide filter through outlets directed towards the human zone.

Table 5.1. Mean concentrations of the target gases collected from the different sampling locations in each chamber at Day 5 to 15 after treatment application, n=9.

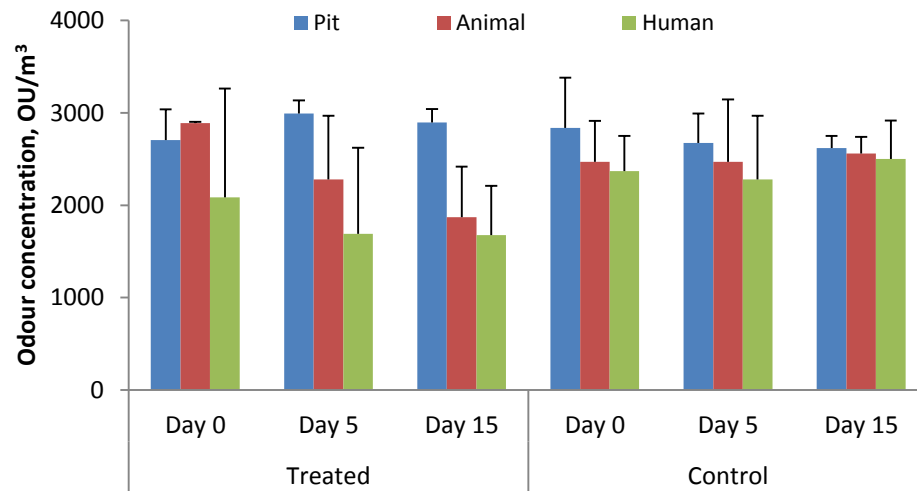
Target Gas	Sampling Location	Mixing		Filtration	
		Treated	Control	Treated	Control
Hydrogen sulphide (ppm)	Pit	9	769	370	385
	Animal	1	54	51	82
	Human	1	43	20	63
Ammonia (ppm)	Pit	21	22	20	22
	Animal	12	11	10	13
	Human	10	10	7	11

5.2.3 Effect on odour concentrations

Due to the limited availability of the olfactometry laboratory at the University of Manitoba, only one batch of samples from mixing tests was sent for odour analysis. These samples were collected at the pit, animal and human levels on the third sampling event (Day 15 after treatment application) of the third trial. Measured odour levels in the treated chamber were slightly lower than in the control chamber especially above the manure pit as shown in Figure 5.13-A. This trend could be attributed to the lower hydrogen sulphide levels observed in the chamber treated with zinc oxide nanoparticles. Six out of ten compounds with the lowest odour detection thresholds (i.e., the strongest odourants) are sulphur-containing compounds (O'Neill and Phillips, 1992). On average, odour concentration in the treated and control chambers was 1960 and 2423 OU/m³, respectively.



A



B

Figure 5.13. Mean (\pm SD) odour concentrations at the pit, animal and human levels in the untreated (control) and treated chambers during the room-scale tests for mixing (A) and filtration (B) methods. No significant change ($P>0.05$) in odour levels was observed after filter installation.

Figure 5.13-B shows the odour concentrations at the different sampling locations in each chamber during the room-scale tests of the filtration method. Prior to the installation of the test filters (Day 0), odour levels in the control and treated chambers were almost the same with average values of 2551 and 2536 OU/m³, respectively. In the control chamber, these levels almost remained the same up to 15 days after the installation of the filter pad only. This trend was observed for the ammonia and hydrogen sulphide levels in this chamber which remained unaffected by the installation of the filter pad over 15 days of monitoring. In contrast, a decrease in odour concentrations at the animal- and human-occupied zones in the treated chamber was observed. Initially, mean odour concentrations at the animal and human levels in the treated chamber were 2888 and 2087 OU/m³, respectively, and were reduced to 2278 and 1689 OU/m³, respectively on Day 5 after zinc oxide filter application. The decrease in odour concentrations especially in the human zone could be attributed to the lower gas levels in this area as a result of the operation of the filter system with zinc oxide nanoparticles. Statistical analysis, however, revealed that the reduction was not significant ($P>0.05$).

5.2.4 Effect on pig performance and manure characteristics

During the entire 30-day trial period of the mixing tests, pigs in the control chamber consumed more water and feed than those in the treated chamber by about 0.2 L/day-pig and 0.04 kg/day-pig, respectively (Table 5.2). Further, daily manure production rate and average daily gain of pigs in the control chamber was slightly higher than those in the treated chamber. However, statistical analysis showed that these differences between the pig performance in the two chambers were not significant ($P>0.05$).

In the filtration tests, the average daily water usage, manure production rate, average daily feed intake, and average daily gain of the pigs in the treated chamber were slightly higher than those in the control chamber by about 0.3 L/day-pig, 0.02 L/day-pig, 0.02 kg/day-pig and 0.01 kg/day-pig, respectively. However, no significant difference between the two chambers was observed for these parameters ($P>0.05$). In both mixing and filtration tests, average daily feed intake followed the same trend as average daily gain. This could be due to the positive correlation between pig's average daily feed intake and average daily gain (NRC, 1987). Thus, the results above indicated that the application of mixing and air filtration methods with zinc oxide nanoparticles had no significant adverse or beneficial effect on pig performance.

Table 5.2. Daily water usage, manure production rate, average daily gain, and average daily feed intake of pigs in the control and treated chambers during the room-scale experiments.

Hog performance parameters	Mixing ¹		Air filtration ¹	
	Treated	Control	Treated	Control
Average daily water usage (L/day-pig)	2.2±0.8	2.4±0.1	2.4±0.7	2.1±0.4
Average daily manure production (L/day-pig)	2.28±0.24	2.33±0.15	2.09±0.05	2.07±0.12
Average daily feed intake (kg/day-pig)	1.70±0.19	1.74±0.14	1.70±0.13	1.68±0.20
Average daily gain (kg/day-pig)	0.79±0.03	0.82±0.05	0.81±0.06	0.80±0.07

¹Mean (± SD) of 3 replicates.

Comparisons between treated and control for both mixing and filtration methods were not significant ($P>0.05$).

Table 5.3 shows the results of the physical and chemical analyses conducted on the treated and untreated manure samples. Manure samples mixed with zinc oxide nanoparticles had lower moisture content than untreated manure samples by about 2.6% on average and correspondingly, had higher percentage of total solids. This observation could not be solely attributed to the mixing of zinc oxide nanoparticle into the manure since the filtration tests wherein the manure was not treated with nanoparticles also showed the same trend. Moisture content of the manure was likely influenced by water addition from drinkers, evaporation and other processes (ASABE, 2005a). Percent solids have positive correlation with most manure elements especially with phosphorus (Racz and Fitzgerald, 2001). This correlation was evident in the results wherein the concentrations of phosphorus as well as calcium, copper, iron, magnesium, manganese, sodium and sulfur in treated manure samples was slightly higher than those in untreated samples. Similar to percent total solids and moisture content, these differences were not statistically significant ($P>0.05$). Furthermore, the application of the treatment did not significantly alter the pH of the manure with values very close to 7.0, which is the reported pH of most swine manure (Chastain et. al., 2000). The soluble salt content of the manure samples as measured through electrical conductivity (EC) was relatively high; this can be attributed to the high levels of salt-based minerals added to the diet (Racz and Fitzgerald, 2001). In addition, the total Kjeldahl Nitrogen (TKN), as an approximation of the total nitrogen in the manure sample (Peters et al., 2003), is the sum of the ammonium-N and organic-N (Chastain, 2000). Ammonium-N could be lost to the air as ammonia through volatilization. In the filtration tests, ammonium-N was about 58% of the total Kjeldahl nitrogen for both samples. In the mixing tests, ammonium-N in the treated samples was about 61% of the total Kjeldahl nitrogen while in the untreated samples was about 66%. The difference, however, was not significant ($P>0.05$).

Table 5.3. Characteristics of manure samples collected from each chamber during the room-scale experiments.

Parameters	Mixing ¹		Air filtration ²	
	Treated	Control ³	Treated	Control ³
Moisture (%)	86.40±3.58	89.00±4.56	84.95±5.02	87.15±3.46
Total Solids (%)	13.60±3.58	10.99±4.57	15.05±5.02	12.85±3.46
Conductivity, EC (uS/cm)	17020±9960	24330±1460	18350±11240	23200±4670
pH (pH)	7.27±0.21	7.09±0.04	6.86±0.21	7.01±0.01
Total Kjeldahl Nitrogen (mg/kg)	9400±2200	8400±1700	12800±3300	12000±2600
Ammonium-N (mg/kg)	5700±1400	5500±1100	7400±1300	7000±1100
Calcium, Ca (mg/kg)	2400±1200	1700±700	3300±400	2700±200
Copper, Cu (mg/kg)	50±28	38±15	74±13	65±14
Iron, Fe (mg/kg)	294±131	223±127	346±25	284±4
Magnesium, Mg (mg/kg)	1600±500	1200±400	1700±400	1500±300
Manganese, Mn (mg/kg)	90±32	69±24	115±22	97±13
Phosphorus, P (mg/kg)	3000±1200	2300±900	3600±800	3000±300
Potassium, K (mg/kg)	4800±1100	4300±900	5100±200	4700±300
Sodium, Na (mg/kg)	1400±300	1300±200	1300±100	1300±200
Sulfur, S (mg/kg)	1600±400	1300±100	1500±400	1300±300
Zinc, Zn (mg/kg)	1848±708 ⁴	194±82	327±35	307±30

¹Mean (±SD) of 3 samples; one sample per trial

²Mean (±SD) of 2 samples collected on Days 15 and 30 of the third trial

³Values were different between two sets of tests. Mixing and filtration tests were conducted at different timeframes and diets could also be different.

⁴Amount of zinc in treated and untreated manure samples during mixing tests was significantly different (P<0.05).

As expected, the installation of a filter system with zinc oxide nanoparticles in the treated chamber had no measurable impact on the characteristics of the manure in the tub. On the other hand, the addition of zinc oxide nanoparticles into the manure slurry (mixing) resulted to a significant increase in the amount of zinc by 1,654 mg/kg (P<0.05). In spite of the increase, the zinc content of the treated slurry was below the toxicity limit (2,800 mg zinc per kilogram) set by the U.S. Environmental Protection Agency (EPA, 1994) for biosolid applications. However, it is important to note that elevated levels of zinc in the soil could pose potential risks to the soil microbial communities and plants. According to Moffett et al. (2003), zinc levels as high as 400 mg/kg had caused a reduction on the bacterial diversity in a loamy sand-textured soil from a

sewage sludge field. Population of earthworms (*Eisenia foetida*) was decreased to 50% in 2 weeks when exposed to 574 – 674 mg zinc per kg of artificial soil (Neuhauser et al., 1985). The decrease in microbial communities in the soil would impede the decomposition of organic matter that is necessary for plant growth. In addition, excessive uptake of zinc oxide from soils by plants results to induced deficiency of iron which is responsible for chlorophyll production. This would eventually lead to reduced yields and stunted growth (Broadley et al., 2007). Radish, for instance, has shown 50% reduction in yield when zinc content in the leaves was around 36 – 1013 mg/kg dry weight (Davies, 1993). A 100 mg/kg soil zinc levels has been lethal to red maple and oak seedlings (Buchauer, 1971). With these effects, a full evaluation of the land application of the zinc oxide-treated manure should be conducted to assess if the treated manure is not expected to result to adverse effects when subsequently applied to lands.

5.3 Cost analysis of application of nanoparticles in swine facilities

A preliminary cost analysis of the application of zinc oxide nanoparticles in swine operations was carried out after completing the room-scale experiments. As summarized in Table 5.4, the main components of the analysis included all the costs associated with the treatment (zinc oxide nanoparticles), material and required equipment, as well as labour and operating costs. The estimates were based on the assumption that the treatment was applied to a 100-head grow-finish room (20 to 110 kg) for one complete growth cycle of about 16 weeks. Based on the estimated weight of pigs per week and typical average manure production rate of 2.27 L/day for pigs weighing less than 68 kg and 6.36 L/day for pigs with 68 kg or more body weight (MWPS, 1993), manure clearing (pit-pulling) events were estimated to be carried out on the 5th, 10th, 12th, 14th and 16th week wherein the volume of manure in the underfloor pits per pit-pulling session would be between 8000 to 9000 L.

For the mixing method, the treatment was applied on the 3rd, 8th, 11th, 13th and 15th week of the 16-week cycle. The first two applications were done at two weeks prior to each pit-pulling session based on the results of the room-scale tests (mixing) where the treatment was found to be effective up to 15 days. In order to have almost the same volume of manure to be treated, the remaining three applications were done a week before each pit-pulling event. It was assumed that for each pit-pulling operation, the manure in the underfloor pits was completely drained. Using an application rate of 3 g of zinc oxide nanoparticles per litre of manure as determined from the room-scale experiments, the total amount of zinc oxide nanoparticles applied in the room for one growth cycle was 68.7 kg (Table 5.4). The duration of each treatment application would be about 1.5 hour for a total of 7.5 hours per cycle. Labour cost per hour was assumed to be CAD\$13.0. In addition, the total cost for the required materials included the cost of containers, weighing scale and funnels. These materials were assumed to have an estimated life span of 5 years. Thus, based on the current production performance of the Canadian swine industry where each sow produces 25 piglets per year, the capital cost per finished pig for a 300-sow barn was estimated to be CAD\$0.01. Summing up all these estimates, the total cost associated with the application of mixing method with zinc oxide nanoparticles in a grow-finish stage of operation was around CAD\$67.2 per finished pig.

Table 5.4. Parameters used in the calculation of the total costs of applying zinc oxide nanoparticles in a grow-finish swine production barn.

Operational information and associated cost	Deployment technique	
	Mixing	Filtration
Application rate	3 g/L	0.28 g/cm ²
Frequency of application per cycle	5	4
Total amount of ZnO applied per room, kg	68.7	4.1
ZnO unit price per kg ¹	87.7	87.7
ZnO cost per pig	66.2	4
Number of hours to apply treatment per cycle, hr	7.5	4
Labour cost per hour, \$/hr	13	13
Labour cost per pig	1	0.5
Total costs for required equipment, \$	370	5930 ²
Estimated life span, yr	5	5
Total cost of required material per pig, \$	-	1.6
Capital cost per pig	0.01	1.77
Estimated energy consumption per year, kWh	-	1871
Energy cost per kWh ³	-	0.1
Operating cost per pig	-	0.02
Total cost per pig	67.2	6.3

All costs in CAD\$

¹based on the current price of NanoActive ZnO (www.nanoscalecorp.com)

²includes estimated cost of installation (\$4000)

³SaskPower rate

For the filtration method, an air filter system with zinc oxide nanoparticles was added to the ventilation air recirculation system of the room. Following the set-up of the room-scale experiments, the recirculation system was composed of a horizontal recirculation duct spanning the length of the room with a vertical duct connected to one end. The filter housing, situated in the vertical duct, had a dimension of 61 cm (L) x 61 cm (W) x 3.2 cm (T) similar to commercial air filters. A new filter loaded with zinc oxide nanoparticles was installed on the first week of the growth period and on the 5th, 10th and 14th week prior to each pit-pulling session of that week. The schedule of pit-pulling operations was similar to that in the mixing method. With the

application rate used in the room-scale experiments (0.28 g/cm^2), a total of 4.1 kg of zinc oxide nanoparticles was required for the 16-week growth cycle. To protect the zinc oxide filter from dust accumulation which may affect its performance, a commercial pre-filter was installed at the start of the cycle and replaced every other week. It was assumed that the total number of hours to prepare and change filters was about 4 hours per cycle. Furthermore, the capital cost per pig included the cost of the recirculation fan, duct, filter housing and its installation cost with an estimated life span of 5 years, and other required materials such as pre-filters, and filter pad and plastic styrene for the zinc oxide filter. The energy consumption of the ventilation air recirculation system per year which was based on average pressure loss, air flow rate, total number of operating hours (assumed to be running continuously throughout the year) and fan/motor/drive efficiency were included in calculating the total operating cost expressed on a per pig basis. Thus, the total cost of adding a filtration system with zinc oxide nanoparticles in a swine grow-finish room was about CAD\$6.3 per finished pig.

The results of the cost study showed that the total costs associated with mixing and filtration methods with zinc oxide nanoparticles were about 40.2 and 3.8%, respectively, of the estimated total cost of CAD\$167.15 for the grow-finish stage of production (MAFRI, 2010). The estimated total cost for applying the treatment was relatively high especially for mixing because the assumptions used in the cost estimation above were based on the findings from the room-scale experiments which were conducted under conditions chosen intentionally to produce extremely high levels of the target gases, i.e., if the treatment was found to be effective under these extreme conditions, then it would work as well under typical barn conditions with lower levels of the target gases expected. Some considerations may be applied in order to lower the cost without substantially affecting its effectiveness in reducing the target gases. In the mixing

method, the total cost could be lowered by reducing the cost of zinc oxide used per pig which constituted about 98% of the total cost (CAD\$66.2 of CAD\$67.2). Zinc oxide cost is dependent on the application rate, and frequency and time of application prior to each pit-pulling session. Thus, by lowering the application rate, for instance, to 1.5 g/L which was also shown to effectively reduce hydrogen sulphide and ammonia levels in semi-pilot scale tests, and applying the treatment 3 times per cycle (instead of 5 times per cycle in the calculations above), the total cost could be reduced drastically from CAD\$67.2 to 20.4 per pig. The same applies to the filtration method; if the frequency of filter installation is reduced to 2 times (i.e. on the 1st and 10th week of the cycle) instead of 4 times, the total cost will be reduced from CAD\$6.3 to 4.1 per pig. It should be noted as well that the zinc oxide nanoparticles used in this study were experimental materials purchased at an extremely high unit price; it has been documented that as wider applications were developed recently for certain nanoparticles, this allowed manufacturers to produce these materials in bulk quantities, thus the unit price for these nanoparticles were drastically reduced. Hence, it is anticipated that the total cost for this treatment could still go down significantly as new applications for nanoparticles are identified.

6 CONCLUSIONS AND RECOMMENDATIONS

In line with the stated objectives of this research, the following conclusions can be drawn based on the results:

- Semi-pilot scale tests indicated that the effectiveness of air filtration with zinc oxide nanoparticles was significantly influenced by filter design, face velocity, and amount of nanoparticles per unit area of the filter while that of the mixing method was dependent on the amount of nanoparticles applied into the slurry.
- Room-scale experiments revealed that the addition of zinc oxide nanoparticles into the slurry reduced gas levels, specifically hydrogen sulphide, at the source (manure pit), resulting to almost undetectable levels at the animal- and human-occupied zones. On the other hand, partial filtration of the gases from the source using a zinc oxide filter installed in a recirculation duct set-up did not decrease the gas levels at the source but could likely reduce the gas concentrations at the animal and human levels to comply with the short-term exposure limit (15 ppm for H₂S). The partial filtration set-up can be made more effective with better capture of gases emitted from the source to pass through the filtration system.
- Pig performance and manure nutrient characteristics were not adversely affected by either mixing or filtration using zinc oxide nanoparticles.
- Cost analysis for a typical 300-sow operation (7500 finished pigs per year) using current cost estimates and application parameters indicated that the implementation of filtration treatment

with zinc oxide nanoparticles would amount to about 3.8% of the total production cost, which was economically more feasible than incorporating zinc oxide into the manure slurry. However, various options are available to further reduce the cost of applying the treatment in an actual swine barn.

Recommendations

- Reaction kinetics of the adsorption of gases to zinc oxide nanoparticles should be fully investigated to further optimize the effectiveness of the treatment. This could be done through specialized imaging and spectroscopic techniques that would examine and assess physical and chemical changes in nanoparticles after exposure to manure gases. These same techniques can also be employed to explore the possibility of regeneration of nanoparticles to enable the recovery and reuse of used nanoparticles, thereby saving cost and reducing the risk of possible release to the environment.
- It was speculated in the mixing method tests that the significant decrease in hydrogen sulphide levels achieved when zinc oxide nanoparticles were mixed with manure samples was due to the antibacterial activity of zinc oxide nanoparticles. It is recommended then to conduct a comprehensive study on the antibacterial effect of zinc oxide on sulphate-reducing bacteria (SRB) and other dominant microorganisms in swine manure.
- Newer types of nanoparticles available in the market and other deployment techniques such as spraying nanoparticles diluted in water and incorporation in biofilters should be evaluated. Effectiveness of nanoparticles in reducing airborne contaminants such as pathogens and viruses should also be tested.

- Based on the results observed in the room-scale tests where zinc oxide nanoparticles were able to reduce hydrogen sulphide levels down to below the detection limit of the analyzer, the use of lower application rates of zinc oxide nanoparticles might also reduce hydrogen sulphide levels below 15 ppm (STEL), which would eventually reduce treatment cost.
- It is recommended to apply these treatment approaches in commercial production rooms in order to conduct a more comprehensive feasibility study.
- In addition to the evaluation of the effect of the treatment on manure nutrient properties, its impact on soil and the environment after subsequent land application of the treated manure should also be investigated comprehensively.

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8 APPENDICES

A. Composition and basic analysis of the standard grow-finish diets.

Table A.1. Formulations of the standard grow-finish diets fed to pigs during the room-scale experiments for both mixing and filtration methods.

Ingredients	Percent of Mixture, %		
	Stage 3 Starter	Grower 1	Grower 2
Barley		16.78	31.05
Wheat	45.76	32.14	18.17
Corn Distillers		13.88	13.52
Soy meal	18.00	0.66	0.26
Shorts		20.46	19.92
Oat Groats	10.00		
Fish Meal	7.21		
Canola Oil	1.50	3.24	3.03
Field Peas		10.56	11.95
Prolac 83	12.05		
SD Blood Cells	2.50		
Mono/ dical	0.80	0.07	0.04
Vitamins	0.600	0.005	0.004
Minerals	0.600	0.006	0.006
Salt	0.30	0.51	0.50
Lysine HCL	0.23	0.03	0.03
Threonine	0.105	0.003	0.002
LS 20	0.10		
Choline Chloride	0.080	0.002	0.002
Methionine	0.070	0.0001	
Limestone	0.05	1.55	1.51
CuSO ₄ *5H ₂ O	0.04		
Tallow (Mixer)		0.09	

Table A.2. Basic analysis of the nutrient content of the grow-finish diets.

Nutrient content	Stage 3 Starter	Grower 1	Grower 2
Crude Protein (min), %	19	18.5	17
Crude Fat (min), %	4	2.5	2.5
Crude Fibre (max), %	3	6	6
Sodium (actual), %	0.20	0.20	0.20
Calcium (actual), %	0.80	0.70	0.60
Phosphorus (actual), %	0.60	0.60	0.55
Vitamin A (min), IU/kg	1200	8000	8000
Vitamin D (min), IU/kg	1500	1000	1000
Vitamin E (min), IU/kg	250	20	20
Zinc (actual), mg/kg	500	150	150
Copper (actual), mg/kg	125	20	20

B. Supplementary experimental data – mixing tests

Table B.1. Mean pH of untreated (control) manure samples and samples mixed with zinc oxide nanoparticles at various application rates and contact time in semi-pilot scale tests for the mixing method, n=3.

Treatment ¹	Day 0 (Initial)	Day 5	Day 10	Day 15
Control	7.3	7.8	8.0	8.0
1.5 g/L	7.4	7.8	8.1	8.1
3 g/L	7.4	7.9	8.1	8.2
6 g/L	7.4	8.2	8.6	8.8
8 g/L	7.4	8.3	8.6	8.9

¹pH levels of each treatment from Day 5 to Day 15 were significantly different ($P<0.05$) from their respective Day 0 values.

C. Supplementary experimental data – filtration tests

Table C.1. Mean pressure drop measured across each filter assembly at different face velocities in semi-pilot scale tests for the filtration method, n=3.

Filter type	Amount of nanoparticles, g	Pressure drop, Pa		
		0.2 m/s	0.5 m/s	0.8 m/s
filter pad only	0	10.6	50.0	94.3
packed bed	30	29.3	137.6	244.6
packed bed	60	55.7	154.6	287.4
packed bed	90	59.4	203.0	342.4
fluidized bed	15	26.8	103.4	220.5
fluidized bed	30	33.2	123.1	267.4
fluidized bed	60	52.1	140.4	280.6

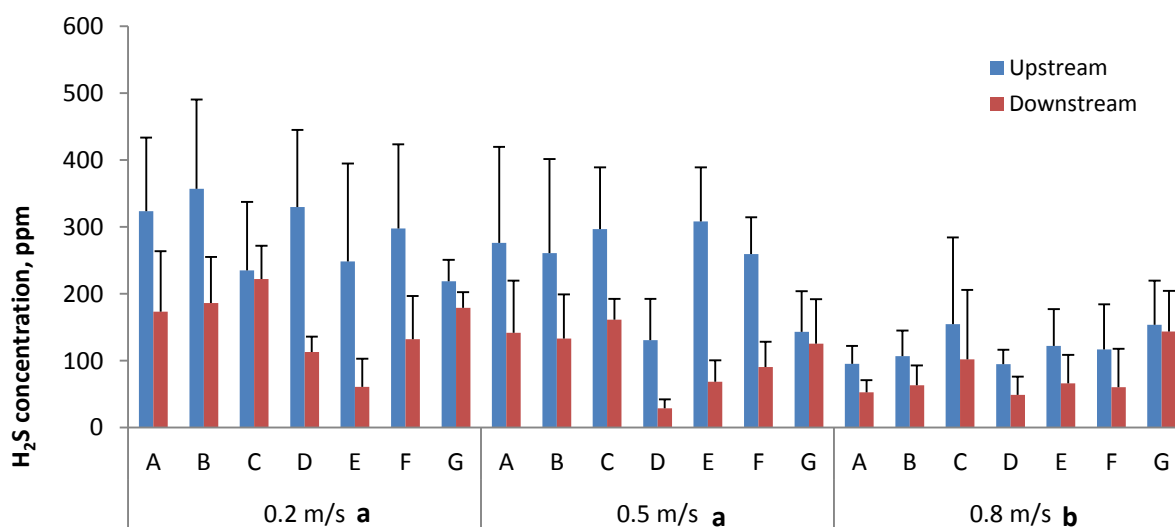


Figure C.1. Mean (\pm SD) actual concentrations of hydrogen sulphide at the upstream and downstream side of packed bed filter with 30 g (A), 60 g (B) and 90 g (C), fluidized bed filter with 15 g (D), 30 g (E) and 60 g (F), and filter pad only (G) in phase 1 tests for the filtration method. Upstream concentrations of face velocities with the same letters are not significantly different ($P > 0.05$).

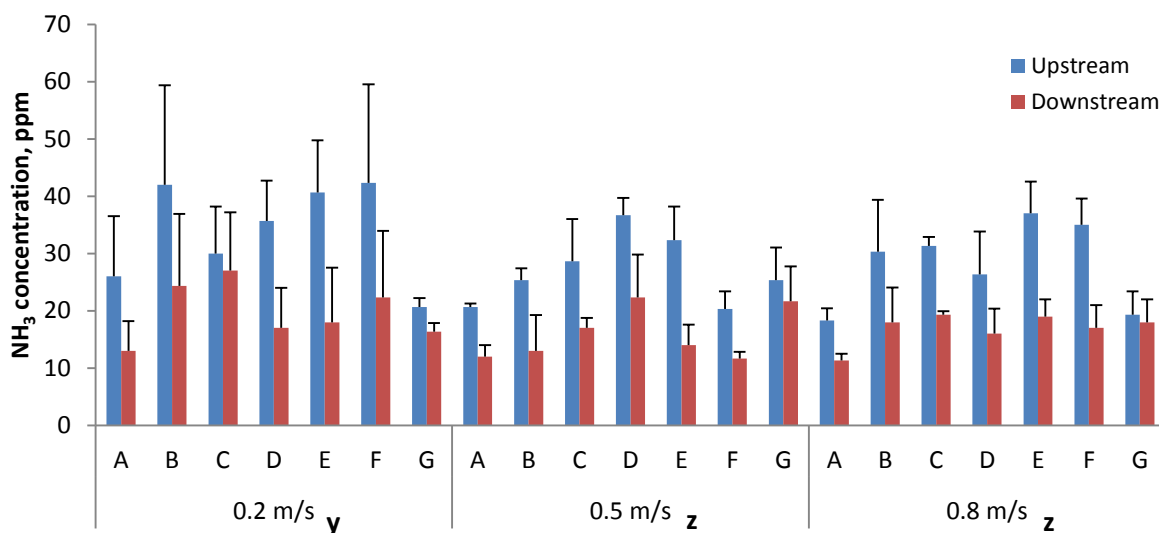


Figure C.2. Mean (\pm SD) actual concentrations of ammonia at the upstream and downstream side of packed bed filter with 30 g (A), 60 g (B) and 90 g (C), fluidized bed filter with 15 g (D), 30 g (E) and 60 g (F), and filter pad only (G) in phase 1 tests for the filtration method. Upstream concentrations of face velocities with the same letters are not significantly different ($P>0.05$).

Table C.2. Mean concentrations of ammonia and hydrogen sulphide at the pit level and at the upstream side of the filter in room-scale experiments for the filtration method, $n=3$.

Sampling points	Ammonia						Hydrogen sulphide					
	Treated			Control			Treated			Control		
	Day 5	Day 10	Day 15	Day 5	Day 10	Day 15	Day 5	Day 10	Day 15	Day 5	Day 10	Day 15
Pit Level	20	21	18	24	23	19	392	379	338	389	397	370
Upstream	14	14	12	18	16	15	185	165	143	205	172	206
% drawn in by the fan	70	67	67	75	70	79	47	44	42	53	43	56